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LXII–LXV. Paper by Mr. N. S. Brommelle and Mr. H. W. L. Phillips . *between pp.* 544 *and* 545

LXVI–LXIX. Paper by Dr. W. A. Wood and Mr. W. A. Rachinger . . *between pp.* 584 *and* 585

LXX–LXXIII. Paper by Mr. A. B. Middleton, Dr. L. B. Pfeil, and Dr. E. C. Rhodes *between pp.* 598 *and* 599

LXXIV–LXXVII. Paper by Mr. R. Chadwick and Mr. W. H. L. Hooper . *between pp.* 616 *and* 617

LXXVIII–LXXXI. Paper by Mr. R. Chadwick, Dr. T. Ll. Richards, and Mr. K. G. Sumner *between pp.* 630 *and* 631

LXXXII–LXXXIII. Paper by Mr. R. Chadwick, Dr. T. Ll. Richards, and Mr. K. G. Sumner *between pp.* 634 *and* 635

LXXXIV–LXXXVII. Paper by Dr. W. Betteridge, Dr. C. Wilson, Mr. M. A. Haughton, and Mr. W. Morgan . . *between pp.* 658 *and* 659

LXXXVIII–LXXXIX. Paper by Dr. V. Kondic and Mr. H. J. Kozlowski . . *between pp.* 666 *and* 667

XC–XCIII. Paper by Mr. G. A. Mellor and Mr. R. W. Ridley . . . *between pp.* 682 *and* 683

XCIV–XCVII. Paper by Mr. G. R. Wilms and Dr. W. A. Wood . . . *between pp.* 698 *and* 699

XCVIII–XCIX. Paper by Dr. H. K. Hardy *between pp.* 714 *and* 715

C–CI. Paper by Mr. W. A. Baker and Mr. A. P. C. Hallowes . *between pp.* 754 *and* 755

CII–CIII. Paper by Dr. G. V. Raynor and Mr. B. R. T. Frost . . *between pp.* 784 *and* 785

CIV–CIX. Paper by Dr. D. E. Adams *between pp.* 816 *and* 817

CX–CXI. Paper by Ing. J. Schoofs *between pp.* 856 *and* 857

CXII–CXV. Mr. R. E. Tricker . . *between pp.* 886 *and* 887

CXVI–CXIX. Paper by M. J. Matter and M. M. Lamourdedieu . . *between pp.* 914 *and* 915

CXX–CXXIII. Paper by Professor A. Portevin and M. M. Dannenmuller . *between pp.* 962 *and* 963

CXXIV–CXXV. Discussion on a paper by Major P. C. Varley . . *between pp.* 1034 *and* 1035

CXXVI–CXXIX. General Discussion on Metallurgical Aspects of Non-Ferrous Metal Melting and Casting of Ingots for Working *between pp.* 1058 *and* 1059

CXXX. Discussion on a paper by Mr. E. F. Emley . . . . . *to face p.* 1110

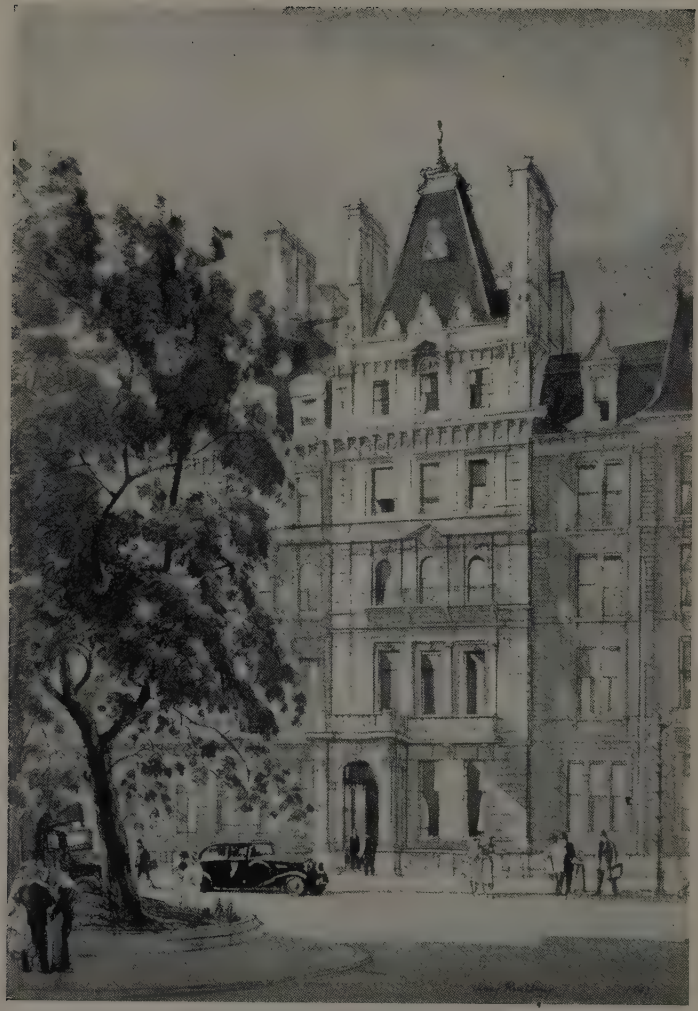
CXXXI. Joint Discussion on papers by Mr. G. R. Wilms and Dr. W. A. Wood and by Dr. W. A. Wood and Mr. W. A. Rachinger . . . *to face p.* 1134

CXXXII–CXXXIII. Discussion on a paper by Mr. A. B. Middleton, Dr. L. B. Pfeil, and Dr. E. C. Rhodes . . *between pp.* 1142 *and* 1143

CXXXIV. Correspondence on a paper by Ing. J. Schoofs . . . . *to face p.* 1166

CXXXV–CXXXVI. Joint Discussion on papers by MM. J. Matter and M. Lamourdedieu and by Mr. W. J. Thomas and Mr. W. A. Fowler . . *between pp.* 1174 *and* 1175

CXXXVII–CXXXVIII. Further Correspondence on a paper by Mr. C. Blazey, Mr. L. Broad, Mr. W. S. Gummer, and Mr. D. B. Thompson *between pp.* 1206 *and* 1207



REPRODUCTION OF A WATER-COLOUR DRAWING, BY HENRY RUSHBURY, R.A., OF 4 GROSVENOR GARDENS, LONDON, S.W.1

This building—one half of which is partly obscured by the tree on the left—contains the headquarters of the Iron and Steel Institute and the Institute of Metals, and their Joint Library and Committee Rooms.

[*Frontispiece, to face p.* xvii.

THE INSTITUTE OF METALS

MINUTES OF PROCEEDINGS

ANNUAL GENERAL MEETING

THE FORTY-FIRST ANNUAL GENERAL MEETING of the Institute of Metals was held in the Hall of the Institution of Mechanical Engineers, Storey's Gate, London, S.W.1, on Wednesday and Thursday, 30 and 31 March, and at 4 Grosvenor Gardens, London, S.W.1, on Friday, 1 April 1949. In the absence of the President, owing to illness, Colonel Sir PAUL GUETERBOCK, K.C.B., D.S.O., M.C., T.D., D.L., M.A., J.P., A.D.C., Past-President, occupied the Chair at the opening of the meeting.

Wednesday, 30 March 1949

The CHAIRMAN notified the members that, owing to illness, the President (Sir ARTHUR SMOUT, J.P.) would be unable to take part in the meeting, and he undertook to convey to the President the best wishes of the meeting for a speedy recovery. He also welcomed members attending the meeting from overseas.

The minutes of the previous General Meeting of the Institute, held in Cambridge from 14 to 17 September 1948, were taken as read and signed by the Chairman.

REPORT OF COUNCIL.

(The Report is printed on pp. 513–520 of this volume.)

The CHAIRMAN (Colonel Sir Paul Gueterbock) : The adoption of this report would normally have been moved by the President so, if I may, I should like to read shortly the comments which he would have made if he had been able to be with us to-day.

The President has asked me to say that the Council is very satisfied with the progress made by the Institute in 1948. The reorganization of the Institute's administration, which began in July 1947, was continued, with the result that the staff was in a far better position to undertake developments. One effect of this was the steady increase in the volume of matter published by the Institute, which will have been noticed by members, in particular, in the monthly *Journal*.

Membership has increased steadily, and on 31 December 1948 it was 3326 members; but this is still, I think you will all agree, a somewhat small proportion of the total number of people connected with the non-ferrous industries. Sir Arthur Smout has asked everybody to co-operate individually and collectively to bring about a large increase during the present year, and the Council hopes that members will respond to this appeal. I would emphasize what Sir Arthur has said several times, namely, that members must put something into the Institute as well as take something out of it. It has to be two-way traffic.

You will have read in the *Journal* with great interest about the very generous offer of Messrs. W. H. A. Robertson and Co., Ltd., of Bedford, of the sum of £100 per annum, for at least seven years, to provide an award or awards to authors of papers published in our *Journal* on engineering aspects of non-ferrous metallurgy. Members may be interested to know that these awards

will take the form of a bronze medal, which has already been designed, and a premium. It is hoped that this additional inducement to members to submit papers on processes and plant will meet with a good response. The Council wants to dispel the impression that only research papers are acceptable for publication by the Institute. That idea is quite erroneous, and papers of a review and descriptive nature are very acceptable.

Members will also have noted with interest that the Council has recently appointed a Metallurgical Engineering Committee, under the Chairmanship of Mr. Donald Campbell, to develop interest in metallurgical engineering in the non-ferrous industry and to promote the study of equipment and instruments used in industrial melting, casting, and working of non-ferrous materials.

The accounts, which our Hon. Treasurer, Mr. Newman, will present to you in a few moments, show that the financial position has very much improved. The past financial year shows a credit balance of £883 against an adverse balance of £2816 for the previous financial year, which I am sure will be regarded as highly satisfactory.

The Institute's interests in various joint activities have been maintained and in particular in the fields of education. You will find that they are referred to in the report.

I think we can say that the year which has closed has been a very satisfactory one, and there are good signs that further progress is being made in the present year to the benefit of the general membership of the Institute.

I formally move that the Report of the Council be adopted.

Dr. C. J. Smithells, M.C. (Vice-President): It gives me great pleasure to second the motion for the adoption of the Report of the Council.

From the remarks of Sir Arthur Smout, which have just been read by the Chairman, it is obvious that the affairs of the Institute are in a satisfactory position.

There are two points to which I should like to draw attention. The first is the very good work which the Institute is doing on the Joint Education Committee and the Committee for National Certificates. The fact that the Institution of Metallurgists is now able to give qualifications is, I think, a great help in the training of the staff which we shall need in the future.

The second point concerns three lines which are tucked away at the end of the report, in which the Council expresses its appreciation of the work of the staff. We have an extremely efficient staff under Colonel Guillan which works hard in looking after the interests of the Institute, and we seldom have an opportunity of saying how much we do in fact appreciate the work which they do. Therefore, in seconding the adoption of this report, I should like to couple with it a hearty vote of thanks to the staff.

The motion for the adoption of the Report of the Council, coupled with a vote of thanks to the staff, was put to the meeting and carried unanimously.

Report of the Honorary Treasurer.

(The Report is printed on pp. 521–522 of this volume.)

Mr. W. A. C. Newman, O.B.E., B.Sc., A.R.S.M., A.R.C.S. (Honorary Treasurer): I have very little to add to the printed report which has already been issued to all members. It will, however, be recalled that at the end of last year it was necessary to meet a deficit by using part of the War-Time Emergency Fund, a fund specially created by the generosity of firms and individuals to meet such emergencies during the war and in the immediate post-war period. Magnificent as the Fund is, it is limited in amount and repeated drawing upon it will naturally lead to an unstable condition. There-

fore, as you are aware, the subscription was raised last year in order to close the gap which threatened to impede the progress of the Institute.

The accounts now before us reflect the result of this major change. We have this year to record an overall excess of income over expenditure of £883. Of this, £677, or 75%, arises directly from excess of income over expenditure in the case of the *Journal* and Special Publications accounts.

A large proportion of the excess of income is due to the sales of publications and to the sale of advertisement space. As the number of copies printed increases, the cost per volume diminishes, and as a result two things emerge : (i) the cost per member of the present services will tend to diminish as membership increases, so that ultimately it will be possible to increase those services, and (ii) the continuing high quality and greater circulation of the publications will attract sales and advertisements which will contribute to an accelerated income from these sources.

Continuing attention is being paid to these matters by the Council, and they would value reciprocal aid from the members, especially in responding to the recent letter from the President asking for missionary efforts among their friends in making known the value of the Institute's work, and in stimulating advertisements in the pages of the *Journal*.

As an inducement to join the Institute it has been decided recently to suspend the payment of an entrance fee during a period of two years.

While the results last year were satisfactory, we must not be lured into complacency. A vigorous company or institute must at times call judiciously on capital in order to initiate further progress, and it may be expected that there may be fluctuations in the accounts year by year as our activities increase. Indeed, the spate of papers now being published resulting from war-time work, coupled with the greater interest in research by an increasing number of workers, which will probably result in a higher steady rate of output of papers than at any previous period, must lead to larger journals and a higher expenditure on publications. It is the policy of the Council, however, that all papers accepted by the Publication Committee shall be printed, and that no artificial horizon or standard of quality shall be created in order merely to keep down costs by diminishing the size of the publications. It may well be that because of intensified activities during the current year, coupled with high costs, the financial position at its close will not be so favourable as in 1947–48, and we may again have to raid the Capital Account. Such an eventuality the Council is willing to face in the interests of the Institute and its members, but they would welcome—indeed, ask for—all the assistance which members can give in the directions I have already indicated.

Over a period of five years the investments of the Institute have increased by £6000. The working capital is the sum of the War-Time Emergency Fund, cash in hand, and certain liquid securities less the liabilities, and on this basis it stood at £7035 at the end of the year. This amount depends, however, on how far and to what extent the War-Time Emergency Fund is called upon. This should be sufficient to finance any exceptional items without interfering with the main capital structure. The total net capital, which is the sum of the working capital, securities, and cash on deposit, amounted to £44,700, an increase of £8400 since 1943. Fluctuations in working capital must occur from time to time, synchronizing with the Institute's activities, but we must be sufficiently flexible to survive these and to be able to maintain a balanced budget, at any rate over a very short period of years. Perhaps I may be excused if I emphasize again that the best insurance in this connection is a maximum membership.

An unusual but pleasing and, I hope, continuing feature in connection with the current year's accounts, is that many more members have paid their subscriptions, mainly by bankers' orders, in the earlier months of the year.

This has reduced very considerably the anxieties of your Secretary and your Treasurer as they have not had to operate on such a narrow margin as before, and this has been most helpful.

In general, the Institute is showing satisfactory financial progress. It is thriving and doing good work. I have tried to indicate directions in which we can achieve greater stability and, at the same time, ensure enhanced benefits of membership. If we have cares by the way we must meet them reasonably with due, but not undue, caution.

I have much pleasure in proposing that the accounts of the Institute for the financial year ended 30 June 1949 be and are hereby adopted.

Mr. A. J. MURPHY, M.Sc. (Vice-President): During the war years your Finance and General Purposes Committee tried, like so many other people, to look forward to the situation as it would be after the war, and anticipated with considerable confidence a spate of papers which would be the flow of communications dammed up by war-time security regulations. That which was not, perhaps, so clearly foreseen was the very great all-round increase in the cost of commodities and services. We certainly have that increased cost all round, but I also have the impression that the flow of papers in increased volume is not really a flood-tide from which there will be a recession. I am inclined to think that we must expect a continued high level of inflow of good papers.

I would emphasize how great a part publications play in our finances. Roughly, the expenditure on publications, comprising the *Journal* and special publications, constitutes 40% of our total expenditure on all activities. It will be seen, therefore, that on the one hand your Council recognizes that the preparation of publications is probably the major activity of the Institute, and, on the other hand, it recognizes how great an effect on our finances any change in the cost of publications must have.

I feel that the keynote of the Hon. Treasurer's report is in the words that the peak of immediate anxiety is probably being approached; and in those circumstances we must all be very content that on the whole the tone of his remarks and report is one of confidence in the future.

It is very gratifying that the increase in subscriptions, which, after long reflection the Council found to be necessary last year, has not resulted in any diminution of membership nor, I believe, in any slackening in the rate of inflow of new members. It is also very pleasing that the Treasurer can say to-day that the situation with regard to the prompt payment of subscriptions is better than it was at the time when he drafted the report which is in our hands.

My impression, which I hope will be that of all the members, is that the Hon. Treasurer's report justifies confidence in the financial future of the Institute, but emphasizes the necessity for the maintenance of constant vigilance.

I have much pleasure in seconding the motion for the adoption of the accounts.

The motion for the adoption of the accounts was put to the meeting and carried unanimously.

RE-ELECTION OF AUDITORS.

It was proposed, seconded, and carried that Messrs. Poppleton and Appleby be re-elected Auditors to the Institute for the ensuing year.

ELECTION OF OFFICERS FOR 1949–50.

The SECRETARY read the names of Officers elected to fill vacancies on the Council for 1949–50, as follows:

President :
Sir ARTHUR SMOUT, J.P.

Vice-Presidents :
Major C. J. P. BALL, D.S.O., M.C.
C. J. SMITHELLS, D.Sc., M.C.

Members of Council :
E. A. BOLTON, M.Sc.
C. H. DAVY
A. G. QUARRELL, D.Sc., Ph.D., A.R.C.S., D.I.C.

The SECRETARY (Lieut.-Colonel S. C. Guillan, T.D.) : In accordance with Article 28, the Council has nominated Mr. H. W. G. HIGNETT, B.Sc., to fill a casual vacancy on the Council occasioned by the resignation of Dr. B. CHALMERS. The Council nominates Mr. Hignett for re-election, in accordance with Article 23(*a*), and unless the names of other candidates are put forward before the conclusion of this meeting, he will be deemed to be elected. Publication of the Council's intention and of members' rights in this connection was made in the news pages of the January 1949 issue of the *Journal*.

RESIGNATION FROM THE COUNCIL.

The CHAIRMAN : Professor LESLIE AITCHISON has, for reasons of ill health, submitted his resignation as an Ordinary Member of Council, and the Council has accepted this resignation with very much regret. In accordance with Article 28, the Council will, in due course, nominate a member to replace him.

Professor Aitchison's retirement is a very great loss to our Council, where his interest and wisdom greatly assisted in the conduct of our affairs.

TERM OF OFFICE OF THE PRESIDENT AND NOMINATION OF SENIOR VICE-PRESIDENT.

The CHAIRMAN : I now come to a matter which has received the very careful attention of your Council, namely, the term of office of the President and the nomination of someone designated to succeed him. The Council reviewed the whole position and what had been the custom for many years, and they considered what should be done within the framework of the rules of the Institute to make a slight alteration in procedure which they felt was in the interests of the Institute and more appropriate to the conditions of to-day. These recommendations have been published in the news columns of the February 1949 issue of the *Journal*, as follows :

" The Council has resolved to recommend to the members that a President should in future normally hold office for one year only. The advantages of this arrangement would be that the Presidency would absorb one individual's full attention for a limited time only, and that it would make it possible for a greater number of members to hold the office.

" It is the Council's intention, at each Annual General Meeting, to notify to the members the name of the ' Senior Vice-President ' (referred to in Article 42), whom it has elected to that position and to make it clear that in due course he will be its nominee for the next vacancy as President. The Senior Vice-President will not hold an additional office, but will be one of the six Vice-Presidents referred to in Article 19. The rights of members, under Article 22, to make their own nominations for President will not, of course, be affected.

" The Council desires that the Senior Vice-President (their nominee for the next vacancy as President) shall be consulted by the President, and have an opportunity to obtain an intimate knowledge of the Institute's affairs for a

full year before the time when it is probable that he will be called on to assume the Presidency. The Senior Vice-President would also take the Chair at all Council meetings and General meetings of the Institute in the absence of the President.

"The Council has elected Mr. H. S. TASKER, B.A. (Vice-President), Chairman of Goodlass Wall and Lead Industries, Ltd., as Senior Vice-President for the year 1949–50, and feels confident that this nomination will meet with the complete and warm approval of the members."

I should like to add my personal view that we could not be more fortunate in this appointment. Mr. Tasker, as you know, holds a very important position in the industry, and has devoted a great deal of time to metallurgical education and to the affairs of this Institute. When I was President of the Institute it was my privilege to work with him as Hon. Treasurer, and nobody could have guided the affairs of the Institute with greater wisdom and success than he did. He was always ready to advise me in matters of policy and so on, and his wisdom made that advice not only extremely valuable to me, but it ensured that I did not get off the rails and let the Institute down too badly.

I have much pleasure in moving that these recommendations of the Council be approved and adopted.

Mr. G. L. BAILEY, M.Sc. (Member): I should like to emphasize one point which the Chairman could hardly emphasize himself, and that is that the office of President of this Institute really does impose a burden on the holder of the position. The President does a lot of work which the ordinary member does not see, and it is unfair to expect him to go on giving so much time to this job. The great advantage of the present recommendation is that it limits the demands which we make on our President to one year, and it will enable more people to take the office than would otherwise be possible.

For that reason, among others, I have much pleasure in seconding this motion.

Dr. RICHARD SELIGMAN (Past-President and Fellow): As one who has held the office of President of the Institute, may I express my keen approval of the decision to limit the term of Presidency to one year. I was conscious at the end of my first year of the growing burden which the Presidency imposed upon me, and all through the second year I felt how much better it would have been if I could have handed over to somebody who came fresh to the office.

I have much pleasure in supporting the motion.

The motion was then put to the meeting and carried unanimously.

CHAIR.

At the request of Colonel Sir Paul Gueterbock, Mr. H. S. TASKER (Senior Vice-President) then took the Chair.

The CHAIRMAN: I should like, first of all, to express my deep appreciation of the honour which has been done me by the Council and by the members of the Institute in electing me to the office of Senior Vice-President. I approach my duties in this office with a real feeling of humility, and a very definite feeling also of inadequacy. I am also quite clear as to the reason for my taking the Chair at the meetings this week. It is really that I am now a substitute for our President, Sir Arthur Smout, whose illness we so much deplore.

During this period of the next year when I shall hold the office of Senior Vice-President, it seems to me that I, and, indeed, in future years those who

hold the position subsequently, will be a sort of cross between an apprentice and a prospective candidate for a political constituency! I have not yet been nominated as President, and I certainly have not yet been elected President. I am here simply as a substitute for Sir Arthur Smout, a substitute called upon, if I may say so, at very short notice. As an apprentice who has not served any part of his term yet, I hope you will forgive any shortcomings which may result from the fact that I have not yet been through the period of training which the Council and the Institute have stipulated for the future!

Vote of Thanks to Retiring Officers.

The Chairman: The following members who have served on the Council are retiring in accordance with the Articles of the Institute: Professor G. Wesley Austin and Mr. W. F. Brazener, Vice-Presidents, and Dr. L. B. Pfeil, Ordinary Member of Council. I want to propose a hearty vote of thanks to those gentlemen for the services which they have rendered during their terms of office. Professor Wesley Austin, in addition to the work he has done for the Institute as Vice-President, was concerned with the arrangements which were made for the meeting last autumn at Cambridge, and its success was undoubtedly due in large part to the work which he did. Mr. Brazener we all know has been a very active and very enthusiastic Chairman of the Local Sections Committee, and the activities of the Local Sections are evidence enough of the fine work which he has done for the Institute in that connection. Dr. Pfeil has for some years carried out the onerous duties of Chairman of the Publication Committee with singular success.

Mr. J. Cartland, M.C., M.Sc. (Vice-President) seconded the motion, which was put to the meeting and carried with acclamation.

Elections of Ordinary Members, Associate Members, and Student Members.

The Secretary announced that since the last General Meeting, the following 113 Ordinary Members, 2 Associate Members, and 122 Student Members had been elected:

Elected on 1 October 1948.

As Ordinary Members.

Bishop, Brian James, Assistant, The Brass and Copper Tube Association, King Edward House, New Street, Birmingham 2.

Bonsack, Walter, Director of Laboratories, Apex Smelting Company, 6700 Grant Avenue, Cleveland 5, O., U.S.A.

de Brouckère, Professor Lucia C. F., Dr. ès Sci., Professor of Chemistry, Faculté de Science, Université Libre de Bruxelles, 50 avenue F. D. Roosevelt, Bruxelles, Belgium.

Cartwright, William Albert, Electrical Engineer, Austral Bronze Company Pty., Ltd., O'Riordan Street, Alexandria, N.S.W., Australia.

Cheng, Chao-Fong, S.B., Resident Metallurgical Engineer, International Nickel Company, Inc., c/o I.C.I. (China), Ltd., 133 Szechuan Road, Shanghai, China.

Durrant, Archibald William, D.S.O., Company Secretary, Rhokana Corporation, Ltd., 11 Old Jewry, London, E.C.2.

Edwards, Owen Graham, Production Superintendent, Austral Bronze Company Pty., Ltd., Alexandria, N.S.W., Australia.

Fishwick, Stanley James, Metallurgist, Thomas Chatwin and Co., Great Tindal Street, Birmingham 16.

Fuidge, Guy Hamilton, B.Sc., Chief Physicist, South Metropolitan Gas Company, 709 Old Kent Road, London, S.E.15.

Goodwin, Edward Charles, Heat-Treatment Superintendent, Armstrong Whitworth and Company (PT), Ltd., Close Works, Gateshead-on-Tyne, Co. Durham.

Hooper, William Henry Lewis, B.Sc., Research Technical Officer (Metallurgist), Imperial Chemical Industries, Ltd., Metals Division, Witton, Birmingham 6.

Le Bailly, Lieut.-Commander (E) Louis Edward Stewart Holland, R.N., Engineer Officer, Royal Navy, Sharpham Park, Walton, near Street, Somerset.

Lindsay, Noel Ker, B.A., B.C.L., Director, British Non-Ferrous Metals Federation, 132 Hagley Road, Birmingham.

McCloud, John Lansford, B.Ch.E., Director of Chemical Engineering and Chemical and Metallurgical Research, Ford Motor Company, Dearborn, Mich., U.S.A.

Marvin, Philip Roger, B.S., Director of Research and Development Engineering, Milwaukee Gas Speciality Company, 722 North Jackson Street, P.O. Box 461, Milwaukee 1, Wis., U.S.A.

Massy-Greene, John Brian, B.A., Manager, Austral Bronze Company Pty., Ltd., Derwent Park Factory, Glenorchy, Hobart, Tasmania, Australia.

Molineux, Arthur Leslie, Assistant Managing Director, Winfields Rolling Mills, Ltd., Icknield Port Road, Birmingham 16.

Reese, John H., B.S., Technical Advisor, Revere Copper and Brass, Inc., Dallas Division, 2200 North Natchez Avenue, Chicago 35, Ill., U.S.A.

Rotherham, Leonard, M.Sc., Head, Metallurgical Department, Royal Aircraft Establishment, Farnborough, Hampshire.

Ryder, Percy, Works Manager, Charles Clifford and Son, Ltd., Birmingham 5.

Saha, G. M., B.Sc., Chemist and Metallurgist, Ordnance Factory Laboratory, P.O. Muradnagar, Dist. Meerut, India.

Schloen, John Henry, Chemical Engineer; Metallurgist, Canadian Copper Refiners, Ltd., P.O. Box 489, Place d'Armes, Montreal 1, Que., Canada.

Smith, Peter Drury, B.Sc., Engineer, The Laurels, The Ridge, Redlynch, Salisbury.

Thexton, John, A.Met., Research Metallurgist, Research and Development Department, The Mond Nickel Company, Ltd., Wiggin Street, Birmingham.

Turner, William Arthur, Partner, W. A. Turner, Jeffrey, and Company, Foundry Consultants, 44 London Road, Royston, Herts.

Walden, William, Works Manager, John Wilkes, Sons, and Mapplebeck, Ltd., Abberley Street, Winson Green, Birmingham 18.

As Associate Member.

Richards, John Taylor, B.S., Sales Engineer, The Beryllium Corporation, Reading, Pa., U.S.A.

As Student Members.

Bailey, Francis Walter John, B.Sc., Research Metallurgist, Research and Development Department, The Mond Nickel Co., Ltd., Wiggin Street, Birmingham 16.

Bullock, William John, Assistant Experimental Officer, A.E.D., Admiralty; attached to Metallurgical Laboratory, M.E.D., H.M. Dockyard, Devonport.

Davies, Dennis, Metallurgical Assistant, The Mint, Birmingham, Ltd., Birmingham.

Entwistle, Kenneth Mercer, M.Sc., Ph.D., Assistant Lecturer, Department of Metallurgy, The University, Manchester.

Farthing, Thomas William, B.A., Student of Metallurgy, Cambridge University.

Gallacher, William, Metallurgical Chemist, 1 Adamson Street, Mossend, Bellshill, Lanarkshire.

Hargreaves, Maxwell Edgar, B.Met.E., Research Officer, Division of Tribophysics, Council for Scientific and Industrial Research, Australia; attached Cavendish Laboratory, Cambridge.

Heaton, William George, B.Sc., Research Metallurgist, Imperial Chemical Industries, Ltd., Metals Division, Witton, Birmingham.

Jones, Richard Maxwell, B.A., lately Student of Metallurgy, Cambridge University.

Melinck, Gerald Montague, Assistant Chemist, Research Department, Alumilite and Alzak, Ltd., Brentwood Road, London, N.W.10.

Skinner, Richard Anthony, B.Sc., Student, 51 Kingswood Road, Tadworth, Surrey.

Elected on 10 November 1948.

As Ordinary Members.

Contractor, G. P., M.Sc., Ph.D., Assistant Director, National Metallurgical Laboratory, Jamshedpur, India.

Cottell, George Arthur, M.Sc., Research Engineer, 24 Fennel Street, Manchester 4.

Delruelle, André, Ing.civil Mines, Administrateur-Directeur, S.A. Métallurgique de Prayon, rue au Rys 20, Prayon-Trooz, Belgium.

Evans, Frederick Aubrey, Assistant Foundry Manager, Wellworthy Piston Rings, Ltd., Lymington, Hampshire.

Fox, Cecil Percy, M.Sc. (Eng.), Research Engineer, The London Electric Wire Company and Smiths, Ltd., London.

Gamwell, Alfred, The Consolidated Dental Manufacturing Company, Ltd., 1a Shamworth Road, Aigburth, Liverpool.

Geerlings, Hendrikus Gerhardus, Dr.Ir., Chief, Metals Research Department, Laboratorium N.V. De Bataafsche Petroleum Maatschappij, Badhuisweg 3, Amsterdam-N., Holland.

Gifford, David Neef, M.B.E., M.A., Manager, Electric Furnace Company, Ltd., Birmingham.

Gupta, Hari Shanker, B.Sc., c/o Hiralal Motilal and Brothers Jawahergunj, Jubbulpore (C.P.), India.

Johnston, Dominick, M.Sc., Lecturer in Metallurgy, Department of Fuel, The University, Leeds.

Mitchell, Albert, General Manager and Secretary, Bede Metal and Chemical Company, Ltd., Hebburn, Co. Durham.

Mondolfo, Professor Lucio F., Dr.Eng., Associate Professor of Metallurgy, Illinois Institute of Technology, 3300 S. Federal Street, Chicago, Ill., U.S.A.

Mott, Professor Nevill Francis, M.A., D.Sc., F.R.S., Professor of Theoretical Physics, University of Bristol, H. H. Wills Physical Laboratory, Royal Fort, Bristol 8.

Reid, William Alexander, B.Sc., Research Engineer, Anti-Attrition Metal Company, 22 Pinkneys Road, Maidenhead, Berkshire.

Urbano, Luis, Executive Secretary, Instituto del Hierro y del Acero, Calle Villanueva 15, Madrid, Spain.

As Student Members.

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Shrivastava, Onkar Dayal, Junior Field Officer (Steel), Controller of Railway Supplies, Railways Board, Ministry of Railways, New Delhi, India.

Smith, Eric George, B.A., Apprentice, Northern Aluminium Company, Ltd., Rogerstone, Monmouthshire.

Sutton, Alan Lee, Student, Clare College, Cambridge.

Taylor, John Welsh, Research Student, Royal Technical College, Glasgow.

Taylor, (Miss) June Audrey, B.A., Research Bursar, British Non-Ferrous Metals Research Association, Euston Street, London, N.W.1.

Elected on 30 December 1948.

As Ordinary Members.

Ashlin, William Henry Sandford, Director, Broom Ashlin Engineering Company, Ltd., Casilla 510, Valparaiso, Chile.

Austin, Derek Tracy, B.Sc., Student Metallurgical Engineer, Queen's University, Kingston, Ont., Canada.

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Gupta, Prabuddhananda, B.A., Foreman, Rolling Mills, Ordnance Factory, Ambarnath, G.I.P., India.

Hérenguel, Jean François Germain, Dr.ès.Sci., Directeur du Service des Recherches, Sté. des Trefileries et Laminoirs du Havre, 9 rue du Moulin, Antony (Seine), France.

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PODMORE, Ronald Frank, Head of Metal Sales and Shipping Department, Roan Antelope Copper Mines, Ltd., and Mufulira Copper Mines, Ltd., Selection Trust Building, Mason's Avenue, London, E.C.2.

ROBSON, Ernest, General Manager, The Manganese Bronze and Brass Company, Ltd., Handford Works, Ipswich, Suffolk.

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SILCOCK, Elfrid, General Manager, The Monotype Corporation, Ltd., Salfords, Redhill, Surrey.

SISCO, Frank Thayer, Director, Alloys of Iron Research, 29 West 39th Street, New York 18, N.Y., U.S.A.

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WILSON, Ernest Perry Bradley, Chemical Engineer, International Combustion, Ltd., Derby.

As Student Members.

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ATKINSON, George Dennis, Student of Metallurgy, King's College, University of Durham, Newcastle-on-Tyne.

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BRIDGER, Edmund Ian, Laboratory Assistant, Imperial Chemical Industries, Ltd., Metals Division, Witton, Birmingham 6.

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CLEWS, Kenneth James, Research Metallurgist, Imperial Chemical Industries, Ltd., Metals Division, Witton, Birmingham 6.

CRAIG, Francis John, B.A., Research Student in Metallurgy, University of Oxford.

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EVANS, Lionel Stanley, Student of Metallurgy, Birmingham University.

FAGG, Dennis Norman, B.Met., Metallurgist, High Duty Alloys, Ltd., Slough, Buckinghamshire.

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JONES, William Victor, Student of Metallurgy, Birmingham University.

LOWE, (Miss) Jean Margaret, Laboratory Assistant, Imperial Chemical Industries, Ltd., Metals Division, Witton, Birmingham 6.

LYNAM, Eric Royston, Laboratory Assistant, Imperial Chemical Industries, Ltd., Metals Division, Witton, Birmingham 6.

LYONS, Peter, Laboratory Assistant, Imperial Chemical Industries, Ltd., Metals Division, Witton, Birmingham 6.

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MUSCOTT, Arthur, Student of Metallurgy, Manchester University.

PATHAK, Bhasker Ramchandra, M.Sc., Research Student, Department of Metallurgy, Manchester University.

PEAKE, Dudley Miller, Assistant Technical Officer, Imperial Chemical Industries, Ltd., Metals Division, Witton, Birmingham 6.

PEARCE, Christopher Bernard, Laboratory Assistant, Imperial Chemical Industries, Ltd., Metals Division, Witton, Birmingham 6.

PEARSON, William Burton, D.F.C., M.A., Research Student in Metallurgy, Oxford University.

PERRIAM, Leonard Thomas, B.A., Research Physicist, Imperial Chemical Industries, Ltd., Metals Division, Witton, Birmingham 6.

PERRY, Geoffrey Samuel, Laboratory Assistant, Imperial Chemical Industries, Ltd., Metals Division, Witton, Birmingham 6.

POWELL, David Ronald, Metallurgical Chemist, Llanelly Steel Company (1907), Ltd., Llanelly, South Wales.

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REID, George Hunter, Laboratory Assistant, Imperial Chemical Industries, Ltd., Metals Division, Witton, Birmingham 6.

REYNOLDS, Jeffrey Alan, Student of Metallurgy, King's College, University of Durham, Newcastle-on-Tyne.

SHAW, Geoffrey James, Student of Metallurgy, Birmingham University.

STANTON, Robert Henry, Student of Metallurgy, Birmingham University.

THWAITES, Colin John, B.Sc., A.R.S.M., Research Metallurgist, British Non-Ferrous Metals Research Association, Euston Street, London, N.W.1.

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WHITHORN, Arnold Charles, Laboratory Assistant, Imperial Chemical Industries, Ltd., Metals Division, Witton, Birmingham 6.
WILSON, Laurence Reginald, Student of Metallurgy, Manchester University.
YAO, Tung-Ping, B.Sc., Research Student in Metallurgy, Birmingham University.

ELECTED ON 22 FEBRUARY 1949.

As Ordinary Members.

ALEXANDER, Ben H., B.S., M.S., D.Sc., Metallurgical Engineer, Sylvania Electric Products, Inc., Bayside, Long Island, N.Y., U.S.A.
BAGGOTT, Eric Raymond, B.Sc., Chief Chemist, William Bate, Ltd., Hospital Street, Walsall, Staffordshire.
BASSETT, Murray Doone, B.Sc., Technical Assistant (Light Alloys), Imperial Chemical Industries, Ltd., Metals Division, Waunarlwydd, near Swansea, Glamorganshire.
BIBBY, Harry, A.M.C.T., Machine Designer, Howard and Bullough, Ltd., Accrington, Lancashire.
BROMFIELD, Thomas Sidney, Managing Director, H. B. Partners, Engineers, 17 May Street, London, W.14.
BURDEN, Haldon, B.Sc., Manager, Carbide Research and Development, Firth-Brown Tools, Ltd., Sheffield.
DANIEL, Gethin Rowland, Director and Group Works Manager, National Smelting Company, Ltd., Avonmouth, Bristol.
DEDRICK, John H., Sc.D., Section Head, Advanced Development Section, Metallurgical Research Laboratories, Sylvania Electric Products, Inc., Bayside, Long Island, N.Y., U.S.A.
EVANS, Arthur, Manager (Light Alloy Sheet and Strip Rolling), Imperial Chemical Industries, Ltd., Metals Division, Waunarlwyydd, near Swansea, Glamorganshire.
GHOSH, Nirmal Kanti, Foreman, Steel Foundry, Nisco, Belur, India.
GRIFFITHS, Harry, Assistant Chief Metallurgist, Research Department, Vickers Armstrong, Ltd. (Supermarine), Hursley Park, Winchester, Hampshire.
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Smith, Stuart Leslie, B.Sc., Technical Officer (Metallurgist), Imperial Chemical Industries, Ltd., Metals Division, Waunarlywdd, near Swansea, Glamorganshire.

Syrén, Carl-Gustaf Erik, Chief Foundry Engineer, Aktiebolaget Nordiska Armaturfabrikerna, Linköping, Sweden.

Thomas, Morgan George, Chief Inspector, Imperial Chemical Industries, Ltd., Metals Division, Waunarlwydd, near Swansea, Glamorganshire.

Thompson, John Graham, B.Chem., Ph.D., Chief, Metallurgy Division, National Bureau of Standards, Washington 25, D.C., U.S.A.

Wellard, Roger, Ing.chim., Dr.-ès-Sci., Chef, Centre d'Études, Société Nationale d'Études et de Construction de Moteurs d'Avions, 22 Quai Gallieni, Suresnes (Seine), France.

Wright, Professor Edwin Chester, M.S., Chem.Eng., Head, Department of Metallurgical Engineering, University of Alabama, Ala., U.S.A.

Young, John Arthur, Development Engineer, Morris Motors, Ltd., Radiators Branch, Woodstock Road, Oxford.

Ziegfeld, Robert Lindley, B.S., Secretary-Treasurer, Lead Industries Association, 420 Lexington Avenue, New York 17, N.Y., U.S.A.

As Student Members.

Agarwal, Prabhu Lal, B.Sc., Assistant Professor of Metallurgy, College of Mining and Metallurgy, Benares Hindu University, U.P., India.

Agarwal, Visheshwer Dayal, B.Sc., Student of Metallurgy, Benares Hindu University, U.P., India.

Barnes, Allan Francis Charles, Student of Metallurgy, Royal School of Mines, London, S.W.7.

Bates, Harold, Student of Metallurgy, University of Manchester.

Billington, Jack Charles, Student of Metallurgy, Royal School of Mines, London, S.W.7.

Bridgstock, Guy, Student of Metallurgy, Royal School of Mines, London, S.W.7.

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Robb, Nicholas, Student of Metallurgy, Royal School of Mines, London, S.W.7.

Robinson, Alan Jeffery, Student of Metallurgy, Royal School of Mines, London, S.W.7.

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Taylor, Brian, Student of Metallurgy, Royal School of Mines, London, S.W.7.

Thomas, Louis Tecwyn Owen, Student of Metallurgy, Birmingham University.

Townend, Norman Hubert, Student of Metallurgy, Royal School of Mines, London, S.W.7.

Ubank, Raymond George, Metallurgical Research Assistant, Bristol Aeroplane Company, Ltd., Bristol.

Walker, Francis Ernest, Student, University College, Swansea, Glamorganshire.

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Wilson, Alan Leslie, Student of Metallurgy, University of Sheffield.

Elected on 21 March 1949.

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Arkinstall, Leonard C., 21 Westfield Hall, Hagley Road, Edgbaston, Birmingham.

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Berry, Brian Exley, M.A., Production Manager, Powder Metallurgy Division, Murex Ltd., Rainham, Essex.

Best, Victor Harold, Managing Director, Calorizing Corporation of Great Britain, Ltd., Babcock House, Farringdon Street, London, E.C.4.

Bullard, Charles Frederick, Metallurgical Engineer, Rendel, Palmer and Tritton, Consulting Engineers, 55 Broadway, London, S.W.1.

Coupland, Ernest, M.Sc., Chief Engineer, Rubery Owen and Co., Ltd., Darlaston.

Croxford-Adams, George Francis, Consulting Engineer, "Chestnut House", Barrowby, near Grantham, Lincolnshire.

Ferrell, Edward Francis, B.S., M.S., Ph.D., Research Engineer, Battelle Memorial Institute, 505 King Avenue, Columbus, O., U.S.A.

George, Anjilivelil George, Engineer, Indian Government Mint, 47 Strand Road, Calcutta, India.

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KEE, William Wardrop, B.Sc., Chief Metallurgist, Enfield Rolling Mills, Ltd., Brimsdown, Enfield, Middlesex.

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LANE, Arthur, Rolling Mill Manager, Enfield Rolling Mills, Ltd., Brimsdown, Enfield, Middlesex.

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MARDELL, Edmund Charles Henry, Chemist, John Walton and Company, Southbury Smelting Works, Enfield, Middlesex.

METZGER, Otto, Dipl.-Ing., Director, Enfield Rolling Mills (Aluminium), Ltd., Brimsdown, Enfield, Middlesex.

NABARRO, Frank Reginald Nunes, M.B.E., M.A., B.Sc., Royal Society Warren Research Fellow, H. H. Wills Physical Laboratory, Royal Fort, Bristol 8.

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SPENCE, Neville Spence, B.Sc., Director of Research and Development, Dominion Magnesium, Ltd., Haley, Ont., Canada.

STRÖM, Bengt Ingemar Vilhelm, Research Engineer, AB Svenska Metalverken, Västerås, Sweden.

SYKES, John, Metallurgist, Enfield Rolling Mills, Ltd., Brimsdown, Enfield, Middlesex.

ZENER, Professor Clarence, Ph.D., Institute for the Study of Metals, University of Chicago, Chicago, Ill., U.S.A.

As Associate Member.

CHILDS, Wylie J., Ph.D., Staff Member, Massachusetts Institute of Technology, Cambridge 39, Mass., U.S.A.

As Student Members.

ADAMS, Gordon Joseph, Student of Metallurgy, Birmingham University.

AERON-THOMAS, Paul, Student of Metallurgy, University College, Swansea, Glamorganshire.

ASHTON, Geoffrey, Junior Technical Assistant, British Thomson–Houston Company, Ltd., Rugby.

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DODRIDGE, Norman Roy, Assistant Experimental Officer, D.S.I.R., Garston, Hertfordshire.

HARRIS, John Noel, Student of Metallurgy, University College, Swansea, Glamorganshire.

JASTRZEBSKI, Klemens Roman, Student of Metallurgy, University College, Swansea, Glamorganshire.

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LEE, John Reginald, Student of Metallurgy, University of Birmingham.

MANNOX, Donald John, B.A., Student of Metallurgy, Cambridge University.

ORCHARD, Gordon Stanley, Student of Metallurgy, Cambridge University.

SMITH, Kenneth Alfred, Metallurgical Laboratory Assistant, William Mills, Ltd., Wednesbury, Staffordshire.

WATERHOUSE, Robert Barry, B.A., Student of Metallurgy, Cambridge University.

WILSON, Terence Harold, B.Sc., Foundry Metallurgist, Ford Motor Company, Ltd., Dagenham, Essex.

AWARD OF THE INSTITUTE OF METALS (PLATINUM) MEDAL FOR 1949.

The CHAIRMAN: I now have a duty to perform for which I want particularly to regard myself as simply a substitute for Sir Arthur Smout, because that duty and pleasure is to award and present the Institute of Metals Medal, and it is a duty which belongs peculiarly, I think, to the office of President.

I am, therefore, if you and Dr. Hume-Rothery will permit me, going to read the words which the President, Sir Arthur Smout, would have used had he been present on this occasion.

"A President, in the course of his term of office, has many and varied duties to perform. When I took over from my predecessor, however, I had not appreciated that some of these duties were of such a pleasing character as the one which it is my good fortune to carry out this morning.

"As members are aware, the Council has awarded the Institute of Metals Medal in platinum for the year 1949 to Dr. William Hume-Rothery in recognition of his outstanding services to the science of non-ferrous metallurgy. This medal has been awarded for the past twelve years in appreciation of outstanding services to our industry, whether on the academic, industrial, or technical side, without regard to race, colour, class, creed or country, and, I might add, sex, for we are proud to count a famous woman metallurgist among the recipients.

"It is a good custom of the Institute not to embarrass those we seek to honour by an unduly long account of their achievements. It is as well, for it would take me a long time to recite all the honours and distinctions which have been showered, and deservedly so, on to-day's distinguished recipient.

"Dr. Hume-Rothery, at a comparatively early age, was elected a Fellow of the Royal Society. His work has covered a wide field in the study of the structure of alloys. On the one hand he has set up a new standard in the determination of the phase diagrams of alloys, by scrupulous attention to the purity of the metals used and the means of alloying without introducing extraneous impurities, by the accurate measurement of temperature, the equally careful control of composition, and by combining examination by X-rays and by the microscope with the use of thermal methods. This combination of methods in the hands of one investigator is very rare. Perhaps it arises from the fact that he was originally a chemist, adopting physical methods later.

"From an examination of a number of alloy systems, selected according to the position of the component metals in the periodic table, he arrived at certain generalizations, now widely known as the 'Hume-Rothery rules'. His work, which was subsequently extended by Westgren and Bradley, has not only made systematic a difficult part of metallography, but furnished physicists with material on which the electron theory of metals has been built up. To that theory Dr. Hume-Rothery has himself made important contributions. His books on 'The Metallic State', published by the Oxford University Press, and his well-known Institute of Metals monographs are standard works.

"Dr. Hume-Rothery has not only made brilliant contributions to scientific knowledge, but—what is of equal importance—he has blazed a trail and, like all the great masters, he has trained men to follow in his steps: the Hume-Rothery School, as we call it. Several members of this school have since distinguished themselves in this field of research, applying and extending Dr. Hume-Rothery's discoveries.

"Dr. Hume-Rothery, I ask you to accept at my hands the Institute of Metals Medal in recognition of your outstanding services to metallurgy. We have admired you as an outstanding example to our profession; a man who, by his grit and determination, has not allowed a serious physical disability to prevent him making the greatest contributions to our science and literature.

"Thus we add yet another illustrious name to our distinguished roll of Platinum Medallists. We are fortunate to have the opportunity through this medal of recognizing outstanding contributors to the non-ferrous metal industry while they are still alive and among us, and thus able to know of our appreciation. Too often in life, alas, I feel we withhold our praise and appreciation until it is too late."

Those are the words of Sir Arthur Smout, and I should only like to add my own sense of admiration and privilege in being the one to hand to you this Medal.

Dr. W. Hume-Rothery, F.R.S. (Member): Mr. Chairman I need not say how much I would thank you for the honour which you have done me to-day. It will be of great encouragement to our work at Oxford. You could not have chosen a more suitable year, because you will know that for nearly the whole of my time at Oxford metallurgy has been an unofficial subject in which I was allowed to do research owing to the kind interest first of Professor Soddy and later of Sir Cyril Hinshelwood. That work has been done in the University where there has been no official metallurgical department, but you will be glad to hear that after twenty-three years the subject is to receive official recognition, and this year the subject of Metallography has been made an official supplementary subject in the University.

It is now twenty-three years since you allowed me to read my first paper before the Institute, and I can still remember the help and encouragement I received from Dr. Desch and from Mrs. Haughton. I think that I shall not be far wrong in saying that Dr. Desch has done a great deal behind the scenes in support of our work, and it is only right that he and Sir Henry Tizard should be thanked for the continued support which has enabled us to proceed steadily with our research work at Oxford, and has made your award possible.

You, Mr. Chairman, have called attention to those who have worked with me, and I have indeed been fortunate in having a long list of research students who have thrown themselves enthusiastically into this work. You will not wish me to refer to them by name, but I should particularly like to mention Dr. Reynolds, of the high-temperature camera, and Dr. Raynor, who has done so much in many directions.

There is sometimes an unhealthy tendency to suggest that English arrangements for conducting research are unsatisfactory, but although they may be far from perfect, there is I think much to be said for our general methods. It is well for the entry into academic research not to be too easy, because the true research worker must be prepared to sacrifice something for the freedom of his life. Outside Oxford we have had help on an extensive scale from the Royal Society, the Department of Scientific and Industrial Research, and from the British Non-Ferrous Metals Research Association over a long period of years. In the years between the wars when the new science of metals was being laid down, I think we may say that the methods adopted in this country justified themselves and we need not be ashamed of them. In all this work, the Institute of Metals has played its part in providing a meeting place for metal men, and as a source of publications.

I hope, therefore, Mr. Chairman, that in awarding this medal you will not feel that you are presenting it merely to the individual who is fortunate enough to have his name inscribed on your Roll. You are presenting it to a large number of other people who have played their part either by direct research, or indirectly by providing a scheme which, when all has been said against it, has enabled research workers in many universities to do the work to which they felt they had been called.

Discussion of Papers.

The following papers were then presented and discussed. In each case a hearty vote of thanks to the authors was proposed by the Chairman and carried with acclamation.

"The Working Behaviour of Phosphorus-Deoxidized Coppers Containing Bismuth", by A. P. C. Hallowes, B.Sc., A.I.M.

"The Damping Capacity of Metals in Transverse Vibration" and "The Effect of Grain-Size on the Damping Capacity of Alpha Brass", by K. M. Entwistle, M.Sc., Ph.D. (Joint Discussion.)

"The Flow of Metal in Tube Extrusion", by C. Blazey, M.Sc., B.Agr.Sci., L. Broad, W. S. Gummer, and D. B. Thompson.

"The Promotion and Acceleration of Metallic Corrosion by Micro-Organisms", by T. Howard Rogers, D.I.C., A.I.M.

The discussions are reported in this volume of the *Journal*.

Thursday, 31 March

At the resumed meeting, held at the Institution of Mechanical Engineers, the Senior Vice-President, Mr. H. S. Tasker, B.A., occupied the Chair.

Symposium on Metallurgical Aspects of Non-Ferrous Metal Melting and Casting of Ingots for Working.

A general discussion, fully reported in this volume of the *Journal*, took place on the following papers:

"Melting and Casting of Non-Ferrous Metals", by G. L. Bailey, M.Sc., F.I.M., and W. A. Baker, B.Sc., F.I.M.

"The Production of Refined-Copper Shapes", by R. H. Waddington.

"Melting and Casting Aluminium Bronze Ingots for Subsequent Working", by A. J. Murphy, M.Sc., F.I.M., and G. T. Callis, B.Sc. Tech., F.I.M.

"The Application of Flux Degassing to Commercially Cast Phosphor Bronze", by N. I. Bond-Williams, B.Sc., A.I.M.

"The Melting and Casting of Brass", by Maurice Cook, D.Sc., Ph.D., F.I.M., and N. F. Fletcher, A.I.M.

"The Melting and Casting of Nickel Silver at the Works of Messrs. Henry Wiggin and Co., Ltd.", by E. J. Bradbury, M.Eng., A.M.I.Mech.E., A.I.M., and P. G. Turner, Assoc. Met.

Dinner-Dance.

A dinner-dance was held in the evening at the Savoy Hotel, London.

Friday, 1 April

The meeting was resumed at the headquarters of the Institute, 4 Grosvenor Gardens, London, S.W.1. The Senior Vice-President, Mr. H. S. Tasker, B.A., occupied the Chair.

Discussion of Papers.

The following papers were presented and discussed. In each case a hearty vote of thanks to the authors was proposed by the Chairman and carried with acclamation.

"The Recovery and Recrystallization of Rolled Aluminium of Commercial Purity", by P. C. Varley, M.B.E., T.D., M.A.

"High-Temperature Tensile Properties of Cast Aluminium–Silicon Alloys and Their Constitutional Significance", by W. I. Pumphrey, M.Sc., and P. H. Jennings, Ph.D.

" A Consideration of the Nature of Brittleness at Temperatures Above the Solidus in Castings and Welds in Aluminium Alloys ", by W. I. Pumphrey, M.Sc., and P. H. Jennings, Ph.D.

" A Consideration of the Nature of Brittleness at Temperatures Below the Solidus in Castings and Welds in Aluminium Alloys ", by W. I. Pumphrey, M.Sc., and D. C. Moore, B.Met., M.Sc.

" The Measurement of Grain-Size of Tungsten and Tungsten Carbide Powders Used in the Manufacture of Hard-Metal ", by H. Burden, B.Sc., and A. Barker, B.Sc., A.R.C.S., A.Inst.P., L.I.M.

The proceedings then terminated.

MAY LECTURE

A General Meeting of the Institute was held at the Royal Geographical Society, Kensington Gore, London, S.W.7, on Wednesday, 25 May 1949, the President, Sir Arthur Smout, J.P., occupying the Chair.

The Minutes of the previous General Meeting, held in London on 30 and 31 March and 1 April 1949, were taken as read and signed by the Chairman.

Election of Ordinary Members, Associate Members, and Student Members.

The Secretary (Lieut.-Colonel S. C. Guillan, T.D.) announced that since the last General Meeting the following 44 Ordinary Members, 2 Associate Members, and 26 Student Members had been elected :

Elected on 14 April 1949.

Ordinary Members.

Bailey, Kenneth George Desplan, Metallurgist, Folland Aircraft, Ltd., Southampton.

Cantrell, John, Metallurgist, The Carborundum Company, Ltd., Manchester.

Cartwright, Leonard Octavius, Assistant Factory Manager, Imperial Chemical Industries, Ltd., Metals Division, Selly Oak, Birmingham.

Charles, Hadyn, Chief Works Inspector, Imperial Chemical Industries, Ltd., Metals Division, Swansea, Glamorganshire.

Gardner, Edmund Paley Starkie, B.Sc., Engineer, The Anglo-Iranian Oil Company, Ltd., London.

Grenfell, William Harold, Production Manager, Imperial Chemical Industries, Ltd., Metals Division, Swansea, Glamorganshire.

Harrison, Thomas, Foundry Supervisor, Serck Radiators, Ltd., Warwick Road, Birmingham 11.

Householder, Leland E., B.S., Assistant Chief Metallurgist, Reynolds Metals Company, Brookfield, Ill., U.S.A.

Humphreys, Olliver William, B.Sc., Manager, The Research Laboratories, General Electric Company, Ltd., Wembley, Middlesex.

Jablonski, Stanislaw, Director of Institute of Metallography and Metal Working, Warsaw, Poland.

Johns, Neil, Production Supervisor, Johnson, Matthey and Company, Ltd., 73–83 Hatton Garden, London, E.C.1.

Kasz, Frank, B.Sc., Metallurgist, The British Aluminium Company, Ltd., Bainsford, Falkirk.

KUNDU, Kishori Mohan, Superintendent, Melting Shop, Indian Government Mint, Calcutta, India.

LARKE, Eustace Charles, Metallurgical Engineer, Research Department, Imperial Chemical Industries, Ltd., Metals Division, Witton, Birmingham.

LAWRENCE, Charles Sydney, Senior Executive Officer, Inspectorate of Armaments, Woolwich.

LEWIS, Harry, B.Sc., Research Metallurgist, The Mond Nickel Company, Ltd., Research and Development Department, Wiggin Street, Birmingham, 16.

MCCREDIE, Francis Ian, B.Sc., Australian Aluminium Company Pty., Ltd., Unwin Street, Granville, N.S.W., Australia.

MATTHEWS, Roy Glyn Linton, Metallurgist, Imperial Chemical Industries, Ltd., Metals Division, Landore, Swansea, Glamorganshire.

NEHRENBERG, Alvin Emery, B.S., Supervisor of Research Laboratory, Crucible Steel Company of America, Harrison, N.J., U.S.A.

PAUL, Nripendra Chandra, M.Sc., Metallurgical Chemist, Laboratory, Ordnance Factory, Ambarnath (G.I.P.), Bombay, India.

PETTERSEN, Alf, M.Sc., Chief Metallurgist, Stavanger Electrostaalverk A/S, Norway.

PRINCE, Richard William, Production Manager, Imperial Chemical Industries, Ltd., Metals Division, Broughton Copper Works, Salford, Manchester.

SMITH, Harry, Director, Brontalloy, Ltd., Drighlington, near Bradford.

SUGGITT, John Percy, Managing Director, Hotray Wires, Ltd., Hotray House, Chester Road, Manchester 15.

TECTOR, Frederick James, B.Eng., Joint General Manager, Manganese Bronze and Brass Company, Ltd., Dock Road, Birkenhead, Cheshire.

VERNON, William Thomas, Tool Room Superintendent, H. M. Hobson, Ltd., Hobson Works, Fordhouses, Wolverhampton.

WHITEHEAD, Derek James, B.Sc., Metallurgical Research Department, Magnesium Elektron, Ltd., Clifton Junction, Manchester.

ZYSS, Jozef-Tadeusz, General Manager, Norfolk Metals, Ltd., Effingham Road, Sheffield 9.

Associate Member.

SCHWARTZBART, Harry, B.S., M.S., Research Metallurgist, National Advisory Committee for Aeronautics. (Mail): 21770 Eaton Rd., Fairview Park 16, O., U.S.A.

Student Members.

ABLETT, John Reginald, Student of Metallurgy, The University, Manchester.

BAILEY, Thomas, Student of Metallurgy, King's College, Newcastle-upon-Tyne.

GOODWIN, Robert James, Student of Metallurgy, Cambridge University.

GREGORY, Peter, Junior Metallurgist, Rotol, Ltd., Gloucester.

L'APPELL, Peter Thomas, Student of Metallurgy, Royal School of Mines, London, S.W.7.

LOCK, Leonard Wallace, B.A., Metallurgist/Technical Assistant, Zinc Development Association, Oxford.

MARSH, Peter Ronald, Student of Metallurgy, The University, Manchester.

MILES, Peter Stewart, Student of Metallurgy, The University, Melbourne, Australia.

MULLERY, Frank, Student of Metallurgy, The University, Birmingham.

PARKES, Eric, Metallurgical Chemist, Fordath Engineering Company, Ltd., West Bromwich.

SAMWAYS, Norman Leonard, Student of Metallurgy, Royal School of Mines, London, S.W.7.

Taylor, Frank Donald, Metallurgist, Imperial Chemical Industries, Ltd., Metals Division, Swansea, Glamorganshire.
Varshney, Raj Prakash, B.A., Student, College of Mining and Metallurgy, Benares Hindu University, Benares, India.
Williams, Brian Edward, Metallurgical Laboratory Assistant, The Mint, Birmingham, Ltd., Birmingham.

Elected on 18 May 1949.

As Ordinary Members.

Åkerlund, Jarl Torc, Metallurgist, A/B W. Dan Bergman, Södertälje, Sweden.
Alexander, Kenneth, Chief Metallurgist, Stokes and Sons Pty., Ltd., Brunswick, Australia.
Bidgood, Ivor Michael, M.Sc., Research Assistant, Ministry of Supply, University College, Cardiff.
Binks, Cornelius John, Foundry Manager, C. Binks, Endive Place, Rhodeswell Road, London, E.14.
Brian, James Gilbert, Assistant Works Manager, Imperial Chemical Industries, Ltd., Metals Division, Broughton Copper Works, Manchester.
Brown, Donald William, B.Sc., Metallurgist, The Morgan Crucible Company, Ltd., Battersea Church Road, London, S.W.11.
Corrêa da Silva, Luiz C., Research Engineer, Institute for Technological Research, São Paulo, Brazil.
Deering, Ernest Charles, B.Sc., Director, Johnson, Matthey and Company, Ltd., Hatton Garden, London, E.C.1.
Degowin, Watson Richard, B.M.E., Metallurgist, The Detroit Testing Laboratory, Detroit 26, Mich., U.S.A.
Gallwey, William Broke Hoppner, Managing Director, British Acheson Electrodes, Ltd., Wincobank, Sheffield.
Hale, Edgar Wilfred, Manager, The Morgan Crucible Company, Ltd., Battersea Church Road, London, S.W.11.
Kowalczyk, Joseph Tomath, Dipl.Ing., Technical Adviser to the General Direction de Fabricaciones Militares, Buenos Aires, Argentina.
Lanchbery, William John, Mechanical Engineer, British Phosphate Commission, Christmas Island, Indian Ocean, via Fremantle, Western Australia.
Patrick, Frederick James, City Librarian, Reference Library, Birmingham 1.
Robson, Harry, Assistant Metallurgist, D. Napier and Sons, Ltd., Acton, London, W.3.
White, Dennis George, B.Sc., A.R.S.M., Metallurgist, Thos. Bolton and Sons, Ltd., Widnes, Lancashire.

As Associate Member.

Sproull, Theodore William, B.S., M.S., Metallurgist, Babcock and Wilcox Company, Barberton, O., U.S.A.

As Student Members.

French, Edward Llewelyn, B.A., Assistant Metallurgist, Joseph Lucas, Ltd., Shaftmoor Lane, Birmingham 28.
Ganguli, Ramapati, Student of Metallurgy, College of Mining and Metallurgy, Benares Hindu University, Benares, India.
Hall, Eric Ogilvie, M.Sc., Physicist, Cavendish Laboratory, Cambridge.
Haslam, Norman, B.A., Student of Metallurgy, Cambridge University.
Lefebvre, George A., Student of Metallurgy, Faculté Polytechnique de Mons, Belgium.

Loeb, Roger, Licence en Droit et Econ. Sci., Metallurgist, Les Alliages d'Etain et Dérivés, 204 Rue Saint Maur, Paris, France.

Lynch, Brian Maurice, Student, Melbourne University, Melbourne, Australia.

McKenny, Basil John, Technical Assistant, John Dale, Ltd., Ridgeview Road, London Colney, Herts.

Mahendra, Balram Kumar, Student of Metallurgy, College of Mining and Metallurgy, Benares Hindu University, Benares, India.

Storer, Roy Alan, Assistant Metallurgist, Joseph Lucas, Ltd., Shaftmoor Lane, Birmingham 11.

Thomson, David Charles, Metallurgist, H. E. Carde and Company, Ltd., Holyhead Road, Wednesbury, Staffordshire.

Witt, Robert H., Metallurgist, Sperry Gyroscope Company, Great Neck, Long Island, N.Y., U.S.A.

May Lecture.

The President then introduced Sir Ernest Appleton, G.B.E., K.C.B., M.A., D.Sc., F.R.S., who delivered the Thirty-Ninth May Lecture on "The Organization and Work of the Department of Scientific and Industrial Research" (see this volume, pp. 973–992).

Dr. S. F. Dorey, C.B.E., Wh.Ex., F.R.S. (Vice-President), proposed, Mr. A. J. Murphy, M.Sc. (Vice-President) seconded, and there was carried with acclamation, a hearty vote of thanks to Sir Edward Appleton for his lecture.

The lecturer was afterwards entertained to dinner by the Council at the Hyde Park Hotel.

ANNUAL AUTUMN MEETING

THE FORTY-FIRST ANNUAL AUTUMN MEETING of the Institute of Metals was held in Paris, by invitation of the Société Française de Métallurgie and the French Non-Ferrous Metallurgical Industries, from 3 to 8 October 1949, the business meeting and sessions for the discussion of papers being held at the Maison de la Chimie, 28 rue St. Dominique.

Monday, 3 October

VISITS.

During the day visits were paid to Versailles and to the Centre National de la Recherche Scientifique at Vitry-sur-Seine.

AUTUMN LECTURE.

In the evening the Twentieth Autumn Lecture was delivered at the Maison de la Chimie by Professor GEORGES CHAUDRON on "Recent French Investigations in the Field of Light Alloys". The lecture is printed in the *Journal* 1949–50, vol. **76**, pp. 1–16. A vote of thanks to the lecturer, proposed by Dr. RICHARD SELIGMAN (Past-President and Fellow) was carried with acclamation.

After the lecture members and their ladies were the guests of the Reception Committee at an informal conversazione.

Tuesday, 4 October

The meeting was resumed at the Maison de la Chimie at 10 a.m., the President, Sir ARTHUR SMOUT, J.P., occupying the Chair.

WELCOME TO PARIS.

General P. NICOLAU (President of the Société Française de Métallurgie), speaking in French: After a separation of thirteen years, characterized, unfortunately, by so much suffering shared by both our countries, France, true to her old tradition as a meeting place, has the happy privilege of receiving a visit from the Institute of Metals, and the Société Française de Métallurgie has the agreeable duty of welcoming you. In the name of my colleagues and in the name of the Reception Committee, which combines representatives of the society and of the French non-ferrous metals industry, I bid you welcome.

To understand what lies behind this seemingly banal formula, I should recall the circumstances in which our society was born. In the spring of 1940 we had to establish between our two countries, in the field of metallurgy, a fuller degree of scientific co-operation to serve our common military aims. Albert Portevin, Pierre Chevenard, Professor Chaudron, M. Dupuy, and I, were given this mission by our Ministry of Munitions, and we were received in London by the Institute of Metals and the Iron and Steel Institute. You may have been a little astonished to find that there was a group of French metallurgists capable of co-operating with you and establishing a permanent liaison, and, acting on your advice, we suggested the creation of a French metallurgical society.

The suggestion was favourably received by our Minister of Munitions, but after the tragic events of June, 1940, it required all the faith and the tenacity

of my colleagues to start such a society, which was born under the German occupation in 1943. It is thus to some extent your own child; and it is this little six-year-old child that welcomes you to-day in what is really a family celebration.

In spite of its youth, this child is well aware of the scientific and technical attainments of your Institute and of the services which you have rendered to metallurgical science, extending well beyond the field of the non-ferrous metals which are your particular concern. Many of us have the honour to be members of your Institute, or have been able to submit work for discussion at your meetings and for publication in your *Journal*, which for 41 years has contained information of great interest to all metallurgists. Its pages have always been open to the metallurgists of France, and in return the ideas and work of French metallurgists have been made known to you.

I hope that your stay with us will enable you to appreciate the warmth of our gratitude, and that behind the smiling face of Paris—less frivolous but, if that be possible, even more friendly than in 1936—you will see France at work, and that you will carry away with you this picture of the relations between your Institute and our society, as being, in the words of Shakespeare, a marriage of two friends whom nothing can separate.

The PRESIDENT: On behalf of the members and their ladies who are enjoying the hospitality of the Société Française de Métallurgie and the French Non-Ferrous Metals Industries this week in Paris, I would thank you, my dear General, for your warm welcome to Paris and for the courteous and kindly way in which you have received us. This I do very sincerely. The hospitality of France to the stranger is proverbial throughout the world, and you are certainly living up to your reputation this week.

When I say how happy we are to be holding our Annual Autumn Meeting this year in Paris, I use no figure of speech, nor do I merely express a courteous phrase. We are delighted to be with so many of our pre-war friends and to find that France still stands for all the things that France has always stood for. A strong France is essential for peace and freedom. We are grateful to France for her faith and steadfastness during those cruel and difficult years which followed the tragedy of June, 1940.

As I am to have the privilege of speaking at your banquet this evening, I shall content myself now by expressing my thanks to you personally, General Nicolau, for the warmth of your welcome and for the great part you yourself have played in making this our Paris Meeting of 1949 the great success we all feel it most certainly will be.

The minutes of the previous General Meeting, held in London on 25 May 1949, were taken as read.

The PRESIDENT welcomed the members to Paris and expressed his pleasure that the meeting was attended by well over 300 members and their ladies, including 22 members from countries other than France and Great Britain. He said that four Honorary Members were present—Professor Dr. C. A. F. Benedicks (*Sweden*), Professor P. A. J. Chevenard (*France*), Professor A. Portevin (*France*), and Dr. J. F. Thompson (*U.S.A.*), and that no fewer than six Honorary Corresponding Members to the Council were attending the meeting, viz. M. Féron (*Belgium*), Professor Chevenard (*France*), Professor Taverner (*South Africa*), Professor Orland (*Spain*), Professor Benedicks (*Sweden*), and Professor von Zeerleder (*Switzerland*). The President added that members were present from Australia, Belgium, Canada, France, Germany, Great Britain, Holland, India, Italy, South Africa, Spain, Sweden, Switzerland, and the United States of America.

NOMINATION OF OFFICERS FOR 1950–51.

The SECRETARY (Lieut.-Colonel S. C. Guillan, T.D.) announced that the following members would retire from the Council at the 1950 Annual General Meeting, as required by the Articles of Association:

President:

Sir ARTHUR SMOUT, J.P.

Past-President:

Lieut.-Colonel Sir JOHN GREENLY, K.C.M.G., C.B.E., M.A.

Vice-President:

JOHN CARTLAND, M.C., M.Sc.

Ordinary Members of Council:

N. P. ALLEN, D.Sc., M.Met.
J. W. JENKIN, Ph.D., B.Sc.
Professor H. O'NEILL, D.Sc., M.Met.
G. V. RAYNOR, D.Sc., D.Phil., M.A.
Professor F. C. THOMPSON, D.Met., M.Sc.

He stated that, in accordance with Articles 22 and 28, the Council had nominated the following members to fill the vacancies:

As President:

H. S. TASKER, B.A.

As Vice-Presidents:

Professor H. O'NEILL, D.Sc., M.Met.
Professor F. C. THOMPSON, D.Met., M.Sc.

As Ordinary Members of Council:

G. L. BAILEY, M.Sc.
HARRY DAVIES.
E. H. JONES.
L. B. PFEIL, O.B.E., D.Sc., A.R.S.M.
G. V. RAYNOR, D.Sc., D.Phil., M.A.

He announced that, in accordance with Article 42, the Council had elected Mr. A. J. MURPHY, M.Sc., as Senior Vice-President for the year 1950–51, and that it was the intention of the Council that Mr. Murphy should be its nominee for the Presidency in the year 1951–52.

The SECRETARY reminded the members of their rights, under Article 22, to make other nominations, if desired, before the end of the meeting.

The PRESIDENT: It is now my pleasurable duty to put before you the Council's recommendation for my successor to the Presidential Chair for the year 1950–51. The Presidency of the Institute is a great honour. It is an honour that carries certain responsibilities, some anxieties, but many joys and great opportunities for service both to the metal industry in general and to one's fellow members in particular. We know full well the qualifications which Mr. TASKER has for the office. He has been a member of the Institute for the past sixteen years; he has served on many of its Committees, and he was a most capable and conscientious Honorary Treasurer, who had

charge of our finances at a critical period in our history. He is a public figure not only in the City of London but in his adopted county of Dorset. Anything that he does, he does well.

Mr. Tasker is Chairman of Goodlass Wall and Lead Industries, Ltd., and other companies connected with the non-ferrous metal industry, and has been connected with that industry in various capacities ever since he left the University of Cambridge. His work on the administration side of our industry is well known and his contribution in that field has been, and indeed is to-day, a very real one. His work for metallurgical education and in raising the general status of the profession is well known and deeply appreciated by all metallurgists throughout the country.

When Mr. Tasker's name was suggested as our President as successor to myself, it was received by the Council with great enthusiasm, and I have every confidence that the Council's recommendation will be fully approved by the members.

Election of Members and Student Members.

The Secretary announced that, since the last General Meeting, the following 48 Ordinary Members and 13 Student Members had been elected :

Elected on 24 June 1949.

As Ordinary Members.

Adam, Erwin Stefan, Mechanical Engineer, S.A. Ad. Saurer, Arbon, Switzerland.

Agte, Curt, Dr.Ing., Engineer, Priper C.32, u Podmokel, Czechoslovakia.

Banyard, David Ronald, B.Sc., M.Sc., Metallurgist, The British Aluminium Company, Ltd., Salisbury House, London Wall, London, E.C.2.

Baxter, J. Martin, Director, P. and W. MacLellan, Ltd., 129 Trongate Street, Glasgow.

Berry, Joseph Wallace, Joint Managing Director, Birmingham Aluminium Castings (1903) Company, Ltd., Birmid Works, Dartmouth Road, Smethwick, Staffordshire.

Brandenberger, Professor Ernst, D.Sc.nat., Professor and Head of the Materials Testing Section, Eidgenössische Technische Hochschule, Zürich, Switzerland.

Brunt, William, General Manager, Brockhouse Castings, Ltd., Hall Street, Wednesfield, Wolverhampton, Staffordshire.

Burke, Joseph Eldrid, B.A., Ph.D., Research Associate, Knolls Atomic Power Laboratory, General Electric Company, Schenectady, N.Y., U.S.A.

Caden, Robert, Experimental Officer, Metals Laboratory, Engineering Department, H.M. Dockyard, Devonport.

Chippindall, Giles Tatlock, Director-General, Posts and Telegraphs, Postmaster-General's Department, Melbourne C.2, Vic., Australia.

Conway, Cyril Gordon, B.Sc., Consulting Engineer, Power Jets (Research and Development), Ltd., 25 Green Street, London, W.1.

Dardel, Yves Marie Pierre, Engineer, Centre de Documentation Sidérurgique, 12 rue de Madrid, Paris 8e, France.

Fisher, George Albert, Jr., B.Sc., Metallurgical Engineer and Manager, International Nickel Company, Inc., St. Louis Technical Section, 810 Ambassador Building, St. Louis 1, Mo., U.S.A.

Ford, Hugh, D.Sc., Ph.D., University Reader and Assistant Professor in Applied Mechanics, Imperial College of Science and Technology, South Kensington, London, S.W.7.

Hall, Kenneth, Managing Director, Northern Aluminium Company, Ltd., Wellington House, Lancaster Place, Strand, London, W.C.2.

HOBBS, John Francis, B.Sc., Technical Officer, Research Department, Imperial Chemical Industries, Ltd., Metals Division, Witton, Birmingham.
LEPSÖE, Professor Robert, M.Sc., Professor of Metallurgy, Norges Tekniske Høgskole, Trondheim, Norway.
LOWLES, Kenneth, Foundry Manager, A. Cohen and Company, Ltd., Craigton Industrial Estate, Barfillan Drive, Cardonald, Glasgow.
MALAMOUD, George, Dipl.Ing., General Manager, Electrode Factory, Buehrle and Company, Oerlikon Machine Tool Works, Zürich, Switzerland.
MASON, Noel Henry, Principal Scientific Officer, Ministry of Supply (Air), Research and Development of Materials Branch, Thames House, London, S.W.1.
DE RHAM, Claude, Technical Director, S.A. des Câbleries et Tréfileries, Cossonay-Gare, Switzerland.
SALTER, John, B.Sc., Assistant Production Manager, The British Aluminium Company, Ltd., Salisbury House, London Wall, London, E.C.2.
SCHÜTZ, Konrad Edwin, Foundry Engineer, Oederlin and Company, Ltd., Baden, Switzerland.
SHENTON, Edward Bertram, Research Chemist, Incandescent Heat Company, Ltd., Cornwall Road, Smethwick, Staffordshire.
SIMS, Robert, B.Sc., Metallurgist, The British Aluminium Company, Ltd., Bank Quay Works, Warrington, Lancashire.

As Student Members.

MACKENZIE, (Miss) Margaret, Student of Metallurgy, King's College, University of Durham, Newcastle-on-Tyne.
UTTERIDGE, William Ronald, Student of Metallurgy, Coventry Technical College, Coventry.
WHITE, Douglas, Student of Metallurgy, Coventry Technical College, Coventry.

ELECTED ON 1 SEPTEMBER.

As Ordinary Members.

BELLIER, Alfred, Ing. Civil des Mines, General Secretary, Société des Mines et Fonderies de Zinc de la Vieille Montagne, 19 rue Richer, Paris 9e, France.
BRAATEN, Amund, Works Manager, Standard Telefon og Kabelfabrik A/S., P.O. Box 749, Oslo, Norway.
CARON, Maurice Clément Casimir, Director, Compagnie Royale Asturienne des Mines, 196 avenue Victor Hugo, Paris 16e, France.
DANNENMULLER, Marc André Jean, Ing. Civil des Mines, Directeur de l'Usine de la Compagnie Française de l'Etain, Annecy (Haute Savoie), France.
HALE, George Ernest, Technical Engineer, Martin Burn, Ltd., 71 Queen Street, London, E.C.4.
KUBASCHEWSKI, Oswald, Dr. phil., Research Scientist, Ministry of Supply, National Physical Laboratory, Teddington, Middlesex.
LUND, Herman Schröder, Managing Director, AB Svenska Aluminiumkompaniet, Kungsgatan 28, Stockholm, Sweden.
MADDEN, Robert C., S.B., Superintendent, Metallurgical Department, Kaiser Company, Inc., P.O. Box 217, Fontana, Calif., U.S.A.
MEAD, Dexter H., Supervisor of Methods, Revere Copper and Brass, Inc., 2200 North Natchez Avenue, Chicago 35, Ill., U.S.A.
MURFITT, George, Works Manager, Metals and Methods, Ltd., Bacon Works, Langley, near Slough, Buckinghamshire.
OSKARSON, Valde, Chief Engineer, AB Svenska Aluminiumkompaniet, Kungsgatan 28, Stockholm, Sweden.

PATANKAR, Muralidhar V., B.Sc., Lecturer in Physical Metallurgy, Indian Institute of Science, Bangalore, India.

PATELL, Dorab Pheroze, B.E., Assistant Engineer, The Associated Cement Companies, Ltd., 1 Queen's Road, Bombay, India.

PILLANS, Charles Stuart Mortimer, Chairman and Managing Director, West Rand Engineering Works (Pty.), Ltd., Little Birmingham, Krugersdorp, Transvaal, South Africa.

RAE, Donald, Personal Assistant to the Managing Director, McKechnie Brothers, Ltd., Rotton Park Street, Birmingham 16.

RENDALL, John Howard, B.Sc., A.R.S.M., Senior Scientific Officer, Metallurgy Division, National Physical Laboratory, Teddington, Middlesex.

RIVIÈRE, Jaime, Director Adjunto, Fábrica de Mieres, S.A., Apartado No. 20, Mieres (Asturias), Spain.

ROBINSON, Ronald William, Senior Experimental Officer, Royal Naval Scientific Service, Metallurgical Laboratory, Engineering Department, H.M. Dockyard, Malta, G.C.

SANDBERG, Sverre, Transmission Line Engineer, AB Svenska Aluminiumkompaniet, Kungsgatan 28, Stockholm, Sweden.

SMITH, Samuel A., Ph.B., M.E., Vice-President, General Cable Corporation, Bayonne, N.J., U.S.A.

STEPHEN, Russell Duncan, Metallurgist, Delfos, Ltd., Lincoln Road, Industrial Sites, Benoni, Transvaal, South Africa.

TAYLOR, Abraham, M.Sc., Ph.D., Physicist, The Mond Nickel Company, Ltd., Wiggin Street, Birmingham 16.

THOMPSON, Arthur Howard, Managing Director, General Galvanizers, Ltd., Wolverhampton.

As Student Members.

BYER, Kenneth George William, Assistant Experimental Officer, Royal Naval Scientific Service, Metallurgical Laboratory, Engineering Department, H.M. Dockyard, Malta, G.C.

CORDNER, George Denis, Research Scholar, University of Melbourne, Melbourne, Vic., Australia.

DARWIN, George Erasmus, B.A., Technical Assistant to the Managing Director, Compound Electro Metals, Ltd., 42 Pall Mall, London, S.W.1.

GIBLIN, John Francis, B.Eng., Metallurgist, British Insulated Callender's Cables, Ltd., Prescot, Lancashire.

HERBST, Noel Frederick, Student of Metallurgy, University of Melbourne, Melbourne, Vic., Australia.

HINES, John, Student of Metallurgy, Coventry Technical College, Coventry.

JAYARAMAN, A., B.Sc., Research Student (mail): Maratturai P.O., Via Kuttalam, Tanjore District, South India.

QUAASS, Stanley Thomas, B.Met.E., Research Student, Metallurgy Department, Melbourne University, Melbourne, Vic., Australia.

SAINSBURY, George Stratford, Spectrographer, J. Stone and Company, Ltd., Charlton, London, S.E.7.

SAWKILL, John, B.Sc., Research Student, Physics Department, King's College, University of Durham, Newcastle-upon-Tyne.

THE INSTITUTE OF METALS (PLATINUM) MEDAL FOR 1950.

The PRESIDENT: It is with the greatest possible pleasure that I announce that the Council has decided that the Platinum Medal of the Institute shall be awarded for 1950 to that most distinguished and illustrious Frenchman, Professor ALBERT PORTEVIN, Honorary Member of the Institute.

Discussion of Papers.

The following papers were presented and discussed. In each case a hearty vote of thanks to the authors was proposed by the Chairman, and carried with acclamation.

"The New Factory of the Société Centrale des Alliages Légers at Issoire (Puy-de-Dôme) for the Working of Light Alloys", by Jean Matter and Marcel Lamourdedieu, and "Some Technical Problems Influencing Production Economy in the Rolling of Aluminium", by W. J. Thomas and W. A. Fowler. (Joint Discussion.)

"Some Effects of Silicon on the Tendency to Cracking in Aluminium–Copper–Magnesium Alloys of High Purity", by W. I. Pumphrey, M.Sc., Ph.D., and D. C. Moore, M.Sc., B.Met.

Visits and Social Functions.

In the afternoon visits were paid to: Le Magnésium Industriel, Levallois; Manufacture d'Armes de Paris (M.A.P.), St. Denis; Laboratories of the Centre National de la Recherche Scientifique, Bellevue; Compagnie Facel-Metallon, Colombes; a Locomotive Testing Plant at Vitry-sur-Seine; and the Michelin pneumatic-tyred train at the Gare de l'Est.

In the evening members and ladies were guests at a banquet given by the Société Française de Métallurgie and the French Non-Ferrous Metallurgical Industries at the Cercle Interallié, 33 Faubourg St.-Honoré.

Wednesday, 5 October

Discussion of Papers.

The meeting was resumed at the Maison de la Chimie at 10 a.m., the President occupying the Chair, and the following papers were presented and discussed. In each case a hearty vote of thanks to the authors was proposed by the Chairman and carried with acclamation.

"Segregation and Liquation of Alloys and Their Application to Non-Ferrous Metallurgy", by Professor Albert Portevin and Marc Dannenmuller.

"Mechanism of Creep in Metals", by G. R. Wilms, B.Met.E., and W. A. Wood, D.Sc., and "Crystallite Theory of Strength of Metals", by W. A. Wood, D.Sc., and W. A. Rachinger, B.Sc. (Joint Discussion.)

Visits.

In the afternoon visits were paid to the Centre Technique de l'Aluminium, Paris; Etablissements Japy, Arceuil; Régie Nationale des Usines Renault, Billancourt; and the cable works of the Société des Tréfileries et Laminoirs du Havre, Saint Maurice.

Official Welcome to Paris.

Later in the afternoon members and ladies attended a reception at the Hôtel-de-Ville when M. de Gaulle welcomed them officially to Paris.

Thursday, 6 October

Visits.

Members took part in an all-day visit to the Chateau de Chantilly, the Fonderies Montupet at Creil, and, by invitation of the Institut de France, the Abbaye de Royaumont.

Friday, 7 October

DISCUSSION OF PAPERS.

The meeting was resumed at the Maison de la Chimie at 10 a.m., with the PRESIDENT in the Chair. The following papers were presented and discussed and in each case a hearty vote of thanks to the authors was proposed by the Chairman and carried with acclamation.

"Observations on the Recrystallization Characteristics of Aluminium–Magnesium–Manganese Alloys", by R. Chadwick, M.A., F.I.M., and W. H. L. Hooper, B.Sc., and "The Effect of Rolling and Annealing Procedures on the Structure and Grain-Size of Aluminium–Copper–Magnesium Alloy Strip", by R. Chadwick, M.A., F.I.M., T. Ll. Richards, B.Sc., Ph.D., F.I.M., and K. G. Sumner, L.I.M.

"Non-Metallic Inclusions in Magnesium-Base Alloys and the Flux-Refining Process", by E. F. Emley, B.Sc.

"Pure Platinum, of High Recrystallization Temperature, Produced by Powder Metallurgy", by A. B. Middleton, A.R.S.M., L. B. Pfeil, O.B.E., D.Sc., A.R.S.M., and E. C. Rhodes, Ph.D., B.Sc.

VOTES OF THANKS.

The PRESIDENT: Experience has taught me that behind every successful enterprise there is what we might term a presiding genius. As I said earlier in the week, this Paris meeting of the autumn of 1949 will linger long in our memories; but, as we all know, meetings such as this, attended as this has been by over three hundred members, with every hour of the day, and often far into the night, crowded with pleasant incident and action, do not just happen. A great deal of preliminary work has to be done to ensure success and to facilitate our happiness, to say nothing of the work which is done during the actual week of the meeting itself.

As I have just said, there is a presiding genius behind it all, and that genius is our friend Dr. EUGÈNE DUPUY, the Secretary-General of the Société Française de Métallurgie, to whom we owe so much. It therefore gives me the greatest possible personal pleasure to move a vote of thanks to Dr. Dupuy for his personal service to the Institute in acting as the Honorary Secretary of this great and most successful meeting in Paris.

The vote of thanks was put to the meeting and carried by acclamation.

The PRESIDENT: The office of President carries with it certain responsibilities, some anxieties, but many joys. I count it amongst the many joys of my office that I have the opportunity, as your President, to thank Mlle. M. SIGWALT for her services in connection with the organization of this meeting. I shall hand to her presently on your behalf a souvenir of the Paris meeting of the autumn of 1949.

We know Mlle. Sigwalt as an experienced organizer, but she can organize and run things, as I can testify, of far greater importance even than the Autumn Meeting of the Institute of Metals. Here I will let you into a secret: I have managed to dig up something of her past, because we in Britain know our friends and have records of Allied war service.

Those of us who were in the service of His Majesty's Government in London during the war are well aware of what went on in France in those long and cruel years which followed June 1940, and Mlle. Sigwalt's name is by no means unknown to us in that connection. She was prominent in the resistance

movement, working secretly towards the great day of liberation. That was a very dangerous game, carried out as it was under the nose of the enemy; a single slip, the slightest indiscretion, a hint of betrayal, and there was only one end, as Mlle. Sigwalt and her friends knew only too well.

Fortunately, all went well and Mlle. Sigwalt has been with us to organize this meeting and to sit with us at this table this morning. We are to-day privileged to honour her and to thank her for her services not only to us this week, and during the weeks of preparation which preceded this meeting, but also to France, to Britain and to the Allied cause.

Her services to Britain were recognized by His Majesty the King when he awarded to her the Special Medal for Bravery which he himself presented to our Allies for personal bravery and devotion to the Allied cause—what has been termed the Allied Civilian Victoria Cross, the greatest honour for bravery and devotion to duty which Britain can offer to any man or woman not born under the Union Jack.

Mlle. M. Sigwalt: I feel sincerely moved by your kind present, which comes to me as a most agreeable surprise. It has been a great pleasure for me to do my best to contribute to the organization of this meeting, which brings happy memories of another meeting organized for the Institute in 1936 by the International Bureau of Aluminium, to which I belonged. I recognize among those present many members who took part in that earlier meeting, and they have not changed very markedly in the past thirteen years, though those years were anything but uneventful. I suppose that such durability is due to the virtue of non-ferrous products! I am not going to make a speech, but I ask you please to accept my very best thanks for your gift.

Mr. H. S. Tasker (Senior Vice-President): As the President has said, so happy, so smoothly run, and so useful a meeting as this does not happen of its own accord. In addition to those who appear on the stage, its success must be due to many who work behind the scenes. I have been asked to propose that the best thanks of the Institute of Metals be and are hereby extended to:

(i) The Société Française de Métallurgie and the French non-ferrous metal industries for their invitation to hold this meeting in Paris, and for their hospitality;

(ii) M. de Gaulle and the Municipal Council of Paris for their reception of members and ladies to Paris and for their welcome;

(iii) The directors of laboratories and works in the Paris area and in the provinces for their invitations, and for their hospitality;

(iv) General P. Nicolau, Chairman of the Reception Committee, Dr. Eugène Dupuy, the Honorary Secretary of the meeting, and all members of the Reception Committee and Ladies Committee for all the services that they have rendered to the Institute in making this meeting a success;

(v) The Directors of L'Aluminium Français for making it possible for members of the staff of the Company to devote much time to the administrative detail of the organization of this meeting;

(vi) All others who have contributed to the success of this meeting.

At our various functions and meetings during this week, it will be obvious to all of you that our President has completely used up all the phrases in the British language (as I would say, rather than English) which express gratitude; all the same, I must use them again in referring to our various friends in France who have helped us so much and made us so happy.

First of all, we want as an Institute to express our appreciation to the Société Française de Métallurgie and to the French Non-Ferrous Metal Industries for

their invitation to come to Paris and join with them during the week of their own meetings, and for the hospitality which we have received from them. I do not need to emphasize to members of the Institute how munificent that hospitality has been, and it has been appreciated more than we can say.

Secondly, we must not forget to express our gratitude and our sense of honour to M. de Gaulle and the Municipal Council of Paris for the reception given to the members and their ladies at the Hôtel de Ville. It was undoubtedly a great privilege to be received there by the Président, and it was also a great pleasure to all of us to see as visitors those magnificent apartments in which we were received.

Thirdly—and this, I think, is very important—we want to express our thanks to the directors of laboratories and works in the Paris area and in the provinces for their invitations to us to visit them and for the way in which we were received. All of us who are connected with factories or institutions of that kind know that visits—and particularly visits in the numbers that accepted these invitations—cannot be arranged without a great deal of trouble and dislocation, but we were all made to feel at home and to feel that we were welcome, and to feel that apparently we were not a nuisance, though I am sure that at times we were.

The Société Française de Métallurgie appointed a Reception Committee, headed by their President, General Nicolau, and assisted by a Ladies Committee, to make all the arrangements for our reception and entertainment. We desire most heartily to thank all those ladies and gentlemen who spent so much time and took so much trouble in caring for our happiness and comfort.

We wish to thank the directors of L'Aluminium Français for placing at our disposal members of their staff who have been able to assist in making the arrangements for this meeting, and to them particularly our thanks are due.

There are many others, unnamed and possibly unknown, who have helped on this occasion, and in an omnibus category I wish to include all those not covered in one or other of the classes which I have already mentioned. Moreover, I should not like to omit the thanks which we of the Institute of Metals should give to Colonel Guillan, Major Moore, and Miss King, of the Institute's permanent staff, for all the work which they have done. It has kept them up for long hours for many days, and we are all most grateful to them for their assiduity in our interests.

I therefore have great pleasure in proposing this resolution.

Mr. D. F. Campbell, M.A., A.R.S.M. (Member of Council), who spoke in French, said in seconding the resolution: I desire to underline the words of Sir Arthur Smout and of Mr. Tasker in saying very sincerely that we thank you for the welcome that you have given to us metallurgists from many countries who have taken part in this meeting of the Institute of Metals here in Paris. Our Institute is old and yours is new, but this is the epoch of youth, and we await with great pleasure a close collaboration between us. I hope that the younger engineers of our two countries are going to come to know one another better. These conferences are very advantageous in promoting contact between the engineers of our two countries.

France has always been a country rich in all that concerns the arts and the sciences, and the inventions of French scientists are very well known. In England since the war we have spent considerable sums on research and on the development in industry of the results obtained in the laboratories. It would be deplorable if we could not collaborate to avoid duplication of effort when there are so many problems to be solved. We ought to have no more mystery and necromancy in our industry; the doors of our works ought to be thrown open, and we should all share in the benefits of research.

The improvement of the working conditions of our workers is also a question to be studied, and we should give each other all the information possible. There are very many things to be done to improve the conditions in our works, and we must fight against dirt and heat and smoke.

We leave Paris with regret. We shall have very pleasant recollections of our Paris meeting, and on behalf of all of us I wish to thank General Nicolau and M. Dupuy for all the hospitality which France has shown us, and the Société Française de Métallurgie in particular. We leave with a determination that collaboration between the French and British metallurgists must be increased to help our two countries and our metallurgical industries.

The votes of thanks were then formally put to the meeting and carried by acclamation.

Professor P A. J. Chevenard (Honorary Corresponding Member to the Council for France): A slight indisposition deprives us of the pleasure of hearing General Nicolau at the end of this meeting. I know that you will be unanimous in regretting his absence and in expressing your best wishes for his speedy recovery. The absence of General Nicolau means that the Past-President of the French society has to speak in place of his successor, and you will lose much by this substitution. There is no need, however, for great eloquence. To adopt the metaphor used earlier by General Nicolau, the Société Française de Métallurgie is a child whose cradle was the Institute of Metals, but it is now six years old, and is able to talk, as long as it does not contradict its parent! This child welcomes you, and expresses the hope that thirteen years will not pass before your next visit. It hopes that with the greater experience that age will bring it will be able to welcome you better on the next occasion, and that it will be possible to draw together more tightly the bonds which unite the metallurgists and metallographers of our two great Western nations, imbued as they are with the same ideals of culture and of liberty.

The President: That terminates this memorable Autumn Meeting.

Osmond Centenary Ceremony.

In the afternoon members attended by invitation a ceremony organized by the Société Française de Métallurgie at the Sorbonne in honour of the centenary of the birth of Floris Osmond (1849–1912), the distinguished French metallographer.

Tours in the Provinces.

At the conclusion of the business sessions, some members undertook one or other of two tours which had been arranged in the provinces. Details of these are as follows:

Tour A.—Comprising visits to the works of the Société Centrale des Alliages Légers (SCAL), and the Société pour le Forgeage et l'Estampage des Alliages Légers (FORGEAL) at Issoire (Puy-de-Dôme); the works of the Manufacture Métallurgique de Gerzat at Clermont-Ferrand: and a tour of the Massif-Central.

Tour B.—Comprising visits to the Fonderie et Forges de Crans, Annecy (Savoie); the works of the Compagnie Française de l'Étain at Annecy-Vovray and a famous Bell Foundry at Annecy; the Laboratoire du Service des Recherches, Compagnie de Produits Chimiques et Electrométallurgiques Alais, Froges et Camargue, Chambéry, and the works of the same Company at St. Jean-de-Maurienne.

SYMPOSIUM ON "METALLURGICAL APPLICATIONS OF THE ELECTRON MICROSCOPE".

A GENERAL MEETING of the Institute of Metals was held at the Royal Institution, Albemarle Street, London, W.1, on Wednesday, 16 November 1949, on the occasion of a Symposium on "Metallurgical Applications of the Electron Microscope", organized by the Institute in association with the Chemical Society, the Faraday Society, the Institute of Physics, the Institution of Electrical Engineers, the Iron and Steel Institute, the Physical Society, and the Royal Microscopical Society.

The thirteen papers presented (Serial Nos. 1193–1205), with a report of the discussion, will be published in a separate volume (*Institute of Metals Monograph and Report Series*, No. 8).

MORNING SESSION: ELECTRON-MICROSCOPE TECHNIQUE.

The President of the Institute of Metals (Sir Arthur Smout, J.P.) occupied the Chair during the morning session, and after some introductory remarks called upon Dr. V. E. Cosslett, the rapporteur, to present the following five papers, which were then discussed:

"The Application of the Electron Microscope in Metallography", by N. P. Allen, D.Sc., M.Met.

"Electron Microscopy in Metallurgy", by Professor Pierre Grivet.

"The Use of the Electron Microscope in Metallurgical Research in Germany During and Since the War", by Dr.-Ing. H. Mahl.

"The Structure of Some Non-Ferrous Alloys as Revealed by the Electron Microscope", by G. L. J. Bailey, Ph.D., F.Inst.P., and Sheila Vernon-Smith.

"A Replica Technique for the Examination of Fracture Surfaces with the Electron Microscope", by J. Nutting, B.Sc., Ph.D., and V. E. Cosslett, M.A., M.Sc., Ph.D.

"The Dry Stripping of Formvar Replicas from Etched Metal Surfaces", by J. Nutting, B.Sc., Ph.D., and V. E. Cosslett, M.A., M.Sc., Ph.D.

"The Progress of Electron Microscopy of Metals in America (Excluding the Light Metals)", by C. M. Schwartz.

AFTERNOON SESSION: METALLURGICAL APPLICATIONS.

The Chair was taken by Dr. F. C. Toy (President of the Institute of Physics).

The Chairman called upon Dr. N. P. Allen to summarize the following six papers, which were then discussed:

"The Microstructure of a Water-Quenched Carburized Iron", by J. Trotter, D. McLean, B.Sc., and C. J. B. Clews, Ph.D.

"Electron Microscopy of Light-Metal Alloys", by Fred Keller.

"Observations on the Age-Hardening Process in an Aluminium–Copper Alloy", by G. L. Bucknell, B.A., and G. A. Geach, M.Sc., Ph.D., F.I.M.

"Elementary Slip Processes in Aluminium as Shown by the Electron Microscope", by Arthur F. Brown, M.A., Ph.D.

"Studies in the Electron Microscopy of Nickel–Chromium Alloys", by B. S. Cooper, B.Sc., F.Inst.P., and G. A. Bassett.

"A Note on the Examination of Metal Powders by the Electron Microscope", by J. I. Morley, A.Met., A.I.M.

Votes of Thanks.

The Chairman proposed, and there were carried by acclamation, the following votes of thanks:

That the best thanks of the Institute be and hereby are extended to:

(*a*) The Managers of the Royal Institution for kindly placing their Lecture Theatre and other accommodation at the disposal of the Institute for this meeting.

(*b*) The authors of all papers presented at the Symposium.

(*c*) The rapporteurs for their introductory addresses.

(*d*) The Councils of the Chemical Society, the Faraday Society, the Institute of Physics, the Institution of Electrical Engineers, the Iron and Steel Institute, the Physical Society, and the Royal Microscopical Society for their interest and help in the organization of this Symposium.

(*e*) The firms and individuals who have provided exhibits and demonstrations.

(*f*) All others who have contributed to the success of the meeting.

Exhibits and Demonstrations.

In connection with the Symposium, an exhibition of apparatus, books, and photographs was arranged in the ante-room to the Lecture Theatre, and there were demonstrations of electron microscopes in operation and of replica-stripping techniques.

The meeting terminated at about 6 p.m.

THE WORKING BEHAVIOUR OF PHOSPHORUS-DEOXIDIZED COPPERS CONTAINING BISMUTH.* 1139

By A. P. C. HALLOWES,† B.Sc., A.I.M., Member.

(Communication from the British Non-Ferrous Metals Research Association.)

Synopsis.

The paper describes a study of the hot and cold working behaviour of bismuth-bearing phosphorus-deoxidized coppers. Non-arsenical coppers containing up to 0·1% bismuth were rolled in laboratory trials, and arsenical and non-arsenical coppers containing up to 0·01% bismuth were fabricated into tubes and strips on a works scale.

An earlier study of the mechanism of bismuth embrittlement of deoxidized coppers indicated that bismuth contents higher than those usually tolerable would not introduce fabricating difficulties if the temperature of hot working, or of annealing prior to cold work, was substantially increased and if intermediate annealing was followed by quenching.

Accordingly, two working schedules were adopted in the works trials, one being representative of the normal practice of the works concerned and the other modified as indicated above. It is shown that the modified schedule permits satisfactory working with bismuth contents considerably higher than would otherwise be permissible, and practical recommendations are made indicating the heat-treatment necessary to avoid embrittlement with deoxidized coppers of various bismuth contents. The bismuth limits are also dependent, in lesser degree, on the severity of the working operations involved.

Laboratory tests on the semi-fabricated coppers illustrate the re-embrittling effect of subsequent heat-treatment or hot working at temperatures lower than those required to retain the bismuth in a harmless condition.

I.—Introduction.

A paper on the theoretical aspect of the Association's research into the bismuth embrittlement of phosphorus-deoxidized copper has already been published.[1] The present account describes a study of the working behaviour of bismuth-bearing phosphorus-deoxidized coppers and confirms that higher bismuth contents can be tolerated if the working schedule is modified in the light of the research on the mechanism of embrittlement.

An account of some small-scale laboratory rolling trials of deoxidized non-arsenical coppers containing up to 0·1% bismuth is given in Section III. Section IV describes industrial-scale trials of the manufacture

* Manuscript received 26 January 1948.

† Investigator, British Non-Ferrous Metals Research Association, London.

of tubes and strips from deoxidized arsenical and non-arsenical coppers containing up to 0·01% bismuth. In these trials, hot-working temperatures and intermediate annealing temperatures, followed by quenching, were (*a*) similar to the normal practice of the works concerned, and (*b*) increased, to minimize bismuth embrittlement.

Section V describes laboratory tests designed to reveal any embrittlement in the semi-finished products and to demonstrate the harmful effect of subsequent hot working at unduly low temperatures or cold working after annealing at similar temperatures.

Further experiments, described in Section VI, illustrate the effect of some variables involved in annealing procedure which are not adequately covered in Sections III–V.

The paper concludes with a brief summary and some practical recommendations for the successful working of deoxidized bismuth-bearing coppers.

II.—Previous Work.

Following earlier work by Blazey [2, 3, 4] and by Archbutt and Prytherch,[5] it was shown by Voce and Hallowes [1] that coppers nominally free from oxygen but containing about 0·002% or more of bismuth were brittle in the temperature range between 400° and 700° C. and at room temperature after annealing in this range. The severity of the brittleness and the range of temperature over which it extended increased with the bismuth content. Slow cooling from annealing temperatures above 700° C. developed brittleness which did not occur if the material was rapidly cooled, and, finally, the annealing temperature above 700° C. at which the brittleness disappeared rose with increase of bismuth content. It was concluded that the solid solubility of bismuth in deoxidized coppers increased with temperature and that serious embrittlement did not occur in either hot or cold working if the procedure were such that most of the bismuth remained in solid solution.

The practical implications of this work are that the permissible bismuth content of deoxidized copper is dependent on : (*a*) the hot-working temperature or, in cold working, the temperature of prior annealing and the rate of cooling after heat-treatment, (*b*) the severity of the working operation to which the material is to be subjected, (*c*) the grain-size of the copper, and (*d*) the presence of minor constituents which may affect the amount of free bismuth available for embrittlement.

In the works trials on deoxidized fire-refined coppers containing bismuth, selenium, and tellurium, already described,[6] it was not possible to assess the individual influence of each element. Attempts to

correlate hot-working behaviour with high-temperature tensile, notched-bar, and bend tests were inconclusive, but cold-working behaviour could be correlated with the results of room-temperature tests.

Cook and Parker [7] studied the effects of bismuth, selenium, and tellurium, added separately and together to cathode copper, and found that bismuth contents up to 0·0035 and 0·0065% (the maximum contents used) in phosphorus-deoxidized non-arsenical and arsenical coppers respectively, had no adverse effects on their hot- and cold-working properties during tube manufacture. Failures occurred in the laboratory when specimens cut from the tubes containing approximately 0·003% bismuth or more were bent at 600° C., and marked reductions occurred at room temperature in the tensile strength and elongation of similar specimens from the arsenical tubes with bismuth contents of 0·005% or more.

III.—Laboratory Rolling Trials.

15-lb. charges of O.R.C. cathode copper were melted under charcoal, deoxidized with phosphor-copper to leave a residual phosphorus content of about 0·04%, and cast into strip ingots, 9 × 4·5 × 1 in. Bismuth metal, in amounts up to 0·1%, was added to the melt before pouring. The bismuth and phosphorus contents of the coppers are shown in Tables I and II.

Each casting was cut into four pieces, two for cold and hot rolling respectively in the as-cast condition, and two for cold rolling after soaking for 1 hr. at 900° C. in an atmosphere of nitrogen, followed by quenching of one and slow cooling of the other. The rolling schedules are also given in Tables I and II, together with the results obtained. The ingots were rolled in one direction only, with no intermediate annealing.

The cold-rolling schedule was completed on all the coppers containing up to about 0·03% bismuth, in spite of some cracking of as-cast material, and heat-treatment prior to rolling had little effect. Edge cracking occurred in some cases with 0·015% bismuth and over, but even the material of highest bismuth content (0·10%) was cold rolled both in the "as-cast" and "quenched from 900° C." conditions, though the strip obtained was badly frayed at the edges.

Hot rolling, commencing at 900° C. and with reheating to temperature between successive passes, gave satisfactory results down to 56% reduction with all bismuth contents up to 0·03%, but the coppers containing 0·05, 0·07, and 0·10% bismuth cracked. Further rolling at lower temperatures indicated brittleness in the region of 450°–550° C.

Table I.—*Cold-Rolling Trials in the Laboratory.*

Rolling Schedule: The following passes were used without any intermediate annealing, but with occasional cooling off when specimens became hot. All the specimens were rolled to strip in one direction only.

Although cracking occurred in a number of cases, the rolling schedule was completed except where otherwise stated.

Pass No.	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Thickness, mm.	22	19·4	17·0	14·6	12·8	11·3	9·6	8·1	6·8	5·4	4·3	3·1	2·3	1·6	1·2	0·8
Reduction, %	0	7	23	34	42	49	56	63	67	76	81	86	90	93	95	97

Mark.	Bi, %.	P, %.	Cold Rolling as Cast.	Cold Rolling After 1 hr. at 900° C. and Quenching in Water.	Cold Rolling After 1 hr. at 900° C. and Slowly Cooling in the Furnace.
JXH1 *	0·00002	0·038	Satisfactory.	Satisfactory.	Satisfactory.
JXH2	0·0023	0·040	,,	,,	,,
JXH9	0·0036	0·037	,,	,,	,,
JXH3	0·0054	0·040	,,	,,	,,
JXH4	0·015	0·039	Slight cracking at 5th pass.	,,	,,
JXH5	0·031	0·040	Cracking commenced at 2nd pass.	,,	Satisfactory. Very slight cracking at 3rd pass.
JXH7	0·057	0·039	Slight edge cracking.	Cracks developed at 1st pass.	Satisfactory. Very slight cracking at 1st and 2nd passes.
JXH8	0·073	0·043	Slight edge cracking.	Serious cracking at 1st pass. Rolling discontinued.†	Slight cracks at 1st pass.
JXH6	0·10	0·040	Cracked at 1st pass.	Cracked at 1st pass. Very poor strip.	Cracked badly at 3rd pass. Rolling discontinued after 4th pass.

* No bismuth addition.

† Cracking comparable with that in the 0·10%-bismuth alloy.

TABLE II.—*Hot-Rolling Trials in the Laboratory.*

Rolling Schedule: Specimens reheated to the stated temperatures in an atmosphere of nitrogen between each pass and rolled in one direction only. Thus, each strip was rolled to 56% reduction at 900° C., and for each subsequent pass the temperature was lowered progressively.

Pass No..	0	1	2	3	4	5	6	7	8	9	10	11	12
Thickness, mm. . . .	22	19·4	17·0	14·6	12·8	11·3	9·6	8·1	6·8	5·4	4·3	3·1	2·3
Reduction, %	0	7	23	34	42	49	56	63	67	76	81	86	90
Mark.	Bi, %.	P, %.	900° C.					680° C.	650° C.	550° C.	500° C.	Not Reheated (below 500° C.).	
JXH1*	0·00002	0·038	Satisfactory.					Sat'f'y.	Sat'f'y.	Sat'f'y.	Sat'f'y.	Sat'f'y.	Sat'f'y.
JXH2	0·0023	0·040	"					"	"	"	"	"	"
JXH9	0·0036	0·037	"					...	...	...	...	...	...
JXH3	0·0054	0·040	"					Sat'f'y.	Sat'f'y.	Sat'f'y.	Sat'f'y.	Split.	...
JXH4	0·015	0·039	"					"	"	"	Split.	...	...
JXH5	0·031	0·040	"					"	"	Split.	...	...	...
JXH7	0·057	0·039	Cracked at 1st pass and eliminated at 2nd pass.					...	...	...	...	...	...
JXH8	0·073	0·043	"	"	"	"		...	...	...	...	...	...
JXH6	0·10	0·040	Cracked badly at 1st pass, eliminated.					...	...	...	...	...	...

* No bismuth addition.

in the coppers containing between 0·005 and 0·03% bismuth, as shown in Table II.

IV.—Manufacturing-Scale Trials.

1. *Preparation of Materials.*

300-lb. charges of O.R.C. copper electro-ingots were melted under charcoal in salamander pots in a coke-fired, forced-draught Morgan tilting furnace and deoxidized with phosphor-copper before addition of the bismuth. In the arsenical series, arsenic was introduced as the element before the bismuth.

A billet, 5 ft. long × 3 in. dia., and a vertically cast cake, 28 × 7·5 × 3 in., were poured from each charge, using salamander tundishes, and moulds dressed with a fluid mixture of vaseline and china clay. Approximately 12 in. was cropped from each end of the billet and 6 in. from the head of the cake.

Twelve melts were prepared with bismuth contents from nil to 0·01% in each of the arsenical and non-arsenical series. The residual phosphorus content, with occasional exceptions in the non-arsenical series, was between 0·03 and 0·05%, and arsenic, when present, lay between 0·3 and 0·4%. Analyses of the remelted electro-ingots, made without bismuth additions, are given in Table III, and the analyses of the billets are included in Table IV; the billet analysis is in each case

Table III.—*Spectrographic Analyses of Castings Without Added Bismuth.*

Element, %.	*Non-Arsenical.* Marks : KAV70 (billet) and KAV71 (strip).	*Arsenical.* Marks : KAV120 (billet) and KAV121 (strip).
Antimony	0·0002	0·001
Arsenic	0·002	0·36 *
Bismuth	0·00005 *	0·0001 *
Cobalt	n.d. (<0·0001)	n.d. (<0·0001)
Iron	0·01	0·001
Lead	0·001	0·0004
Phosphorus	0·046 *	0·040 *
Silicon	n.d. (<0·008)	n.d. (<0·008)
Manganese	0·005	0·001
Nickel	0·0006	0·0006
Silver	0·004	0·004
Tin	0·0005	0·0005
Zinc	n.d. (<0·001)	n.d. (<0·001)
Tellurium	n.d. (<0·004)	n.d. (<0·004)

* Chemical determination.
n.d. = not detected; the limit of detection is indicated in brackets.

TABLE IV.—*Drawing Behaviour of Phosphorus-Deoxidized Copper Tubes Containing Bismuth.*

The Table records significant cracking and failures.

Mark.	Composition, %.			Intermediately Annealed at 650° C. During Manufacture.	Intermediately Annealed at 750° C. During Manufacture.
	Bi	P	As		
				Non-Arsenical.	
KAV 70*	0·00005	0·046	...	Satisfactory at all stages.	Satisfactory at all stages.
KAV 94	0·0005	0·040	...		
KAV 74	0·0011	0·048	...		
KAV 76	0·0015	0·046	...		
KAV 78	0·0020	0·038	...		
KAV108	0·0026	0·032	...		
KAV 82	0·0030	0·045	...		
KAV106	0·0035	0·042	...		
KAV 88	0·0040	0·026	...		
KAV 90	0·0051	0·039	...		
KAV 92	0·0060	0·040	...	Both tubes cracked on 2nd shoulder and broke up in following draw. Discarded.	One of 2 tubes cracked on 2nd tag, but drawn satisfactorily.
KAV104	0·0075	0·043	...		
KAV102	0·010	0·035	...		
				Arsenical.	
KAV120	0·0001	0·040	0·36	Satisfactory at all stages.	Satisfactory at all stages.
KAV118	0·0006	0·049	0·36		
KAV116	0·0011	0·047	0·31		
KAV114	0·0016	0·048	0·35		
KAV112	0·0022	0·040	0·35		
KAV122	0·0027	0·043	0·36		
KAV124	0·0031	0·049	0·34	1 of 2 tubes cracked on 1st tag, but drawn satisfactorily.	
KAV126	0·0035	0·043	0·33	Both tubes cracked on 1st tag and 1 on 2nd tag, but drawn satisfactorily.	
KAV128	0·0040	0·045	0·36	1 of 2 tubes cracked on 2nd tag, but drawn satisfactorily.	
KAV130	0·0051	0·044	0·37		
KAV132	0·0062	0·043	0·39	Both tubes cracked on 1st and 2nd tags, but drawn satisfactorily.	Both tubes cracked on 1st tag and 1 on 2nd tag, but drawn satisfactorily.
KAV134	0·0075	0·044	0·38		
KAV136	0·0092	0·043	0·41		

Sequence of Operations.—The sequence of operations was: shell 3–3·2 in. O.D., 0·375 in. wall; cold shouldered; mandrel drawn to 2·44 in. O.D., 0·25 in. wall; annealed and quenched, one half at 650° C. and the other at 750° C.; cold shouldered; mandrel drawn to 1·91 in. O.D., 0·14 in. wall; annealed and quenched as before; cold shouldered; mandrel drawn to 1·44 in. O.D., 0·094 in. wall; cold tagged; plug drawn to 1·25 in. O.D., 0·0625 in. wall; cold tagged; plug drawn to 1·125 in. O.D., 0·0625 in. wall.

Annealing.—Annealing was for 10 min. at temperature; tubes were quenched approximately 2½ min. after removal from muffle; quenching temperature visually estimated at 550°–600° C. and 600°–650° C. respectively for 650° and 750° C. anneals; tubes pickled 5 min. in 10% sulphuric acid after annealing.

* No bismuth addition.

the same as that of the cake poured from the same charge. Analyses of all the castings showed the amounts of each impurity to be similar to those reported in Table III.*

* With the following exceptions: Sb and Mn occasionally 0·005% in the arsenical coppers. Fe regularly between 0·0005 and 0·003% in the non-arsenical coppers. Pb usually 0·0004% in both series.

2. *Working Operations.*

(a) *Tube Manufacture.*

(i) *Hot Piercing of Billets.*—After heating to 900° C. for 1 hr., the billets were pierced on a rotary piercer of the Mannesman type. The shells were 7–8 ft. long × 3–3·2 in. external dia. (tapered) × 0·375 in. wall thickness. A slight temperature drop occurred during piercing, which occupied about 30 sec., and the shells cooled some 100°–200° C. while being restamped before quenching from about 750° C.

Every billet provided a sound tube shell on piercing, with the single exception of the arsenical copper with the highest bismuth content (0·0092%), in which fine cracking occurred; this did not prevent subsequent drawing.

(ii) *Tube Drawing.*—The shells were drawn to tubes 1·125 in. external dia. × 0·0625 in. wall thickness in five reductions with two intermediate anneals, the first three reductions being by mandrel and the last two by plug drawing. The tubes were halved after the first reduction and each half given the same reductions during drawing, but one half was intermediately annealed at 650° C. (the usual temperature at the mill in question) and the other at 750° C. throughout the operations; each anneal was followed by quenching. Prior to the mandrel draws, the tubes were "cold shouldered" or compressed at the end to fit the mandrel, and cold shouldering was replaced by "tagging", a more severe form of end compression, before plug drawing.

The behaviour of the tubes during drawing is summarized in Table IV. Higher bismuth contents were tolerable in both the arsenical and non-arsenical coppers when the intermediate annealing temperature was raised to 750° C., although it will be seen from the footnote to Table IV that the actual quenching temperatures were considerably lower than the annealing temperatures. Of the tubes annealed at 750° C. only those of highest bismuth content (0·01%) cracked, and this near the end of the schedule. Of those annealed at 650° C. the tubes of both varieties of copper with bismuth contents exceeding 0·005% cracked badly, and the arsenical coppers cracked less seriously and somewhat inconsistently with bismuth contents as low as 0·003%.

Lengths of the tubes containing up to 0·003% bismuth in both the arsenical and non-arsenical series intermediately annealed at 650° C. were re-annealed at and quenched from temperatures of 550° and 600° C. and then redrawn in three passes, without further annealing, to 0·625 in. external dia. and 0·0313 in. wall thickness. The first reduction was by mandrel and the others by plug drawing. Cold shouldering and

tagging operations again preceded the mandrel and plug draws respectively. All the tubes were drawn successfully with the exception of the highest bismuth content (0·003%) in each series, which cracked on tagging.

(b) *Rolling of Cakes.*

Half of each cake was soaked for 45 min. at 850°–950° C. and hot rolled from 3 in. to 0·75 in. thickness in 3 passes at an initial temperature which did not fall below 820° C. The strips were air cooled from about 750° C. and then reduced cold to a final thickness of 0·4 in. in 2 passes, 0·75 to 0·6 in., and 0·6 to 0·4 in. Halves of two of the non-arsenical cakes—one containing 0·0035%, the other 0·0074% bismuth —were quenched from 850° C. and cold rolled to 0·4 in. in three 50% reductions, with intermediate annealing at 900° C. followed by quenching between each.

During hot rolling, only slight edge cracking, unrelated to bismuth content, occurred on a few materials, and no cracking was observed during the cold reductions which followed. The two cakes reduced by cold rolling only, following high-temperature quenching, were uncracked.

3. *Grain-Size of Tubes and Strips.*

The importance of grain-size was not fully appreciated when these manufacturing trials were carried out, but in view of later evidence [1] the grain-sizes of a representative selection of the finished tubes and strips were measured in the annealed condition. Corresponding tubes and strips from the same charge were chosen for the determinations, and the materials were annealed for ½ hr. at 550°, 600°, 650°, and 750° C. in accordance with the annealing schedules used prior to the laboratory tests described in Section V. Tests showed that 10-min. anneals as used during drawing gave grain-sizes similar to those obtained after ½ hr.

The results indicated that there was little difference between the grain-sizes of the arsenical and non-arsenical coppers after similar working and annealing treatment, and no significant variation with bismuth content. The grain-sizes of tubes and strips were similar for a given final annealing treatment and appeared to be a function of the final annealing temperature, there being no apparent effect attributable to earlier thermal history. Since the laboratory and manufacturing anneals were both preceded by severe cold work, it may be inferred that the grain-sizes of the coppers after annealing in manufacture were defined by the annealing temperature, and that the relationship

between annealing temperature and grain-size was approximately as follows :

Annealing Temperature, ° C.	Grain-Size, $\sqrt{\text{Area}}$ of Average Grain, mm.
550°	0·02
650°	0·04
750°	0·07

V.—Laboratory Tests on the Tubes and Strips.

1. *Flattening and Doubling-Over Tests on Tubes.*

Specimens of the tubes were flattened to contact by hammering for a length of about 2 in. at one end, and this end of the tube was then doubled back through 180°, again hammering to contact.

(a) *Tubes Annealed at* 650° *or* 750° *C. During Manufacture.*

The results of tests on the as-drawn tubes and on sample lengths annealed in the laboratory for ½ hr. at, and quenched from, 550°, 650°, and 750° C. are given in Table V.

(i) *As Drawn.*—Cracking occurred indiscriminately (including one of the bismuth-free arsenical tubes) and was probably influenced more by the degree of hardening during drawing than by the bismuth content or the annealing treatment in manufacture.

(ii) *Annealed and Quenched.*—Tubes re-annealed and quenched from the annealing temperatures used in manufacture showed no embrittlement, but re-annealing at lower temperatures caused embrittlement in some cases. The arsenical coppers were not re-embrittled when a manufacturing anneal of 750° C. had been used, but both varieties of copper showed the effect when this anneal was at 650° C.; the non-arsenical coppers were also re-embrittled despite annealing at 750° C. during drawing.

On the whole, therefore, the non-arsenical coppers appeared more sensitive to bismuth embrittlement than the arsenical, though this was somewhat at variance with the behaviour of the coppers in tube drawing.

In neither the arsenical nor the non-arsenical series was there a single instance of cracking of annealed tubing containing 0·0026% bismuth or less; the same amount of bismuth was permissible for any of the severe cold-working operations in manufacture.

TABLE V.—*Flattening and Doubling-Over Tests on Phosphorus-Deoxidized Copper Tubes Containing Bismuth.*

The Table records significant cracking.

Mark.	Composition, %.			As Drawn.		Manufacturing Anneals at 650° C.	Manufacturing Anneals at 750° C.
				Manufacturing Anneals at:		Annealed at 550° C.* in Laboratory.	Annealed at 550° C.* in Laboratory.
	Bi	P	As	650° C.	750° C.		
Non-Arsenical Coppers.							
KAV 70†	0·00005	0·046	...	...	...	...	...
KAV 94	0·0005	0·040	...	*CD* (1)	...	...	...
KAV 74	0·0011	0·048	...	*CF*	*CF*	...	...
KAV 76	0·0015	0·046	...	...	...	...	...
KAV 78	0·0020	0·038	...	...	*CF* (1)	...	...
KAV108	0·0026	0·032	...	...	...	...	...
KAV 82	0·0030	0·045	...	...	...	*CF*/*CD*	*CD* (1)
KAV106	0·0035	0·042	...	...	*CD* (1)	...	...
KAV 88	0·0040	0·026	...	...	...	...	...
KAV 90	0·0051	0·039	...	...	...	...	*CD* (1)
KAV 92	0·0060	0·040	...	...	...	*TD*	*CF*/*CD*
KAV104	0·0075	0·043	...	...	...	*TD*	*CF*
KAV102	0·010	0·035	...	...	...	*TD*	*CF*
Arsenical Coppers.							
KAV120†	0·0001	0·040	0·36	*CD* (1)	...	...	...
KAV118	0·0006	0·049	0·36	*CD* (1)	...	...	...
KAV116	0·0011	0·047	0·31	...	*CF* (1)	...	...
KAV114	0·0016	0·048	0·35	...	*CF*	...	...
KAV112	0·0022	0·040	0·35	...	...	...	...
KAV122	0·0027	0·043	0·36	...	...	...	...
KAV124	0·0031	0·049	0·34	*CF* (1)	...	...	...
KAV126	0·0035	0·043	0·33	*CF* (1)	...	*CF*/*CD*	...
KAV128	0·0040	0·045	0·36	*CD* (1)	*CF* (1)	...	...
KAV130	0·0051	0·044	0·37	*SF*	*CF* (1)	*CF* (1)	...
KAV132	0·0062	0·043	0·39	*CF*	...	...	...
KAV134	0·0075	0·044	0·38	*CF*	*CF*	...	...
KAV136	0·0092	0·043	0·41	*CF*	*CF*	*CF* (1)	...

* All tubes annealed at 650° or 750° C. in the laboratory were flattened and doubled-over successfully except those of non-arsenical copper containing 0·006% or more bismuth which had received manufacturing anneals at 750° C.; these tubes cracked on flattening.

† No bismuth addition.

Code.

CF = cracked on flattening.
CD = cracked on doubling-over.
SF = split open on flattening.
TD = tubes discarded at early stage of drawing.
(1) = one of two tubes cracked; in all other cases of failure, both tubes cracked.

(b) *Tubes Containing up to* 0·003% *Bismuth, Annealed at* 550° *or* 600° *C. Prior to Further Drawing.*

Duplicate specimens from tubes annealed at 600° C. before further drawing (see p. 8) were annealed for 30 min. at (*a*) 550° C. and (*b*) 600° C. and quenched. Single specimens from tubes annealed at 550° C. prior to redrawing were re-annealed for 30 min. at 550° C. and quenched.

Every sample passed the flattening and doubling test without cracking.

2. *Bend Tests on Tubes.*

Tubes with up to 0·003% bismuth were tested in the "quarter-hard" condition, in which temper tubing is normally supplied for such purposes as domestic water services. Tubes annealed at 550° C. during manufacture were re-annealed at the same temperature, quenched, and hollow sunk 0·031 in. on the diameter. 30-in. lengths of these "quarter-hard" tubes were bent through 90° over a 1·75-in. radius in a standard tube-bending machine. All the tubes were successfully bent without cracking.

Hot bend tests were also made at 550° C. 12-in. samples from each "quarter-hard" tube were filled with sand and annealed for 1 hr. at 550° C.; each was rapidly removed from the furnace and bent through 90° on a heated former of 1·5-in. radius. The tubes of highest bismuth content (0·003%) in both the arsenical and non-arsenical series cracked during these tests. Tubes containing 0·0025% bismuth passed the test.

VI.—The Influence of Some Other Variables in the Heat-Treatment of Deoxidized Coppers Containing Bismuth.

The preceding Sections have been concerned primarily with hot-working and annealing temperatures, but other features of annealing practice which have been shown [1] in small-scale laboratory tests to influence the degree of embrittlement of deoxidized bismuth-bearing coppers are the annealing atmosphere, the rate of cooling from the annealing temperature, and transfer of bismuth from copper of higher bismuth content to copper of lower bismuth content during annealing.

Experiments were made, using the coppers produced in the works trials, to examine the influence of these variables.

It has already been shown [1] that thin strips (0·03 in.) of non-arsenical copper are less brittle after annealing in air (in the brittle range) than after bright annealing, but that the effect is not perceptible with thicker-section specimens (0·4 in.). In the present work, both arsenical and non-arsenical coppers were tested and were found to behave similarly, the oxidizing atmosphere having some beneficial effect on the

thin strips, but no effect which could be attributed to the annealing atmosphere was observed for the thicker sections.

1. *Rate of Cooling from the Annealing Temperature.*

Notched-bar specimens were annealed in air at 750° C. for 30 min. and cooled (*a*) by quenching in water, (*b*) by withdrawal from the furnace into the air, and (*c*) by cooling slowly in the furnace. The air-cooled specimens were wired together into two bundles with about 12 specimens in each, so that their rate of cooling would more nearly approach that of a larger object; the specimens cooled in the furnace were in the brittle range between 700° and 400° C. for 2½ hr. and were cooled from 400° C. to room temperature in a further 10 hr.

The effect of cooling the coppers at these different rates through the embrittling temperature range is shown in Table VI. Quenching from 750° C. produced ductile material throughout the whole range of bismuth contents used (with the exception of the highest in the arsenical series, 0·0092%), but slow furnace cooling induced embrittlement when the bismuth content exceeded about 0·0025% in both the arsenical and non-arsenical series. Although the notched-bar values were still high, particularly in the arsenical coppers, all values under about 95 ft.lb. provided specimens broken on impact. Air cooling of these relatively small masses gave lowered test values when the bismuth contents were greater than about 0·006%, non-arsenical, and 0·0035%, arsenical.

It is concluded that deoxidized coppers containing not more than about 0·0025% bismuth are ductile after annealing at 750° C. irrespective of the rate of cooling. Coppers with bismuth contents in excess of this should preferably be quenched.

2. *Transfer of Bismuth.*

In the earlier work,[1] bismuth-free copper was embrittled by transfer of bismuth from coppers containing 0·075 and 0·1% bismuth, and the present tests were designed to show whether this effect occurred on annealing in proximity to coppers of lower bismuth content. Strips of deoxidized bismuth-free copper, 0·03 in. thick, were annealed in a 95 : 5 nitrogen–hydrogen atmosphere, separated from, but in close proximity to, similar deoxidized copper strips containing 0·01% bismuth. The reverse-bend-test results in Table VII show that bismuth transfer and embrittlement occurred in both arsenical and non-arsenical coppers and confirm that this effect can have practical significance in bright annealing thin sections near others having bismuth contents of the order discussed in this paper.

TABLE VI.—*The Effect on Notched-Bar Value of Rate of Cooling Through the Embrittling Temperature Range.*

Non-Arsenical.						Arsenical.						
Mark.	Composition, %.		Notched-Bar Value (ft.lb.). Annealed at 750° C. in Air for 30 min.			Mark.	Composition, %.			Notched-Bar Value (ft.lb.). Annealed at 750° C. in Air for 30 min.		
	Bi	P	Quenched.	Air Cooled.	Furnace Cooled.		Bi	P	As	Quenched.	Air Cooled.	Furnace Cooled.
KAV 67*	0·00007	0·044	103	119	119	KAV121*	0·0001	0·040	0·36	112	119	111
KAV 95	0·0005	0·040	106	119	115	KAV119	0·0006	0·049	0·36	112	119	112
KAV 75	0·0011	0·048	112	119	119	...	...	...	...	...	...	...
KAV 77	0·0015	0·046	114	119	119	KAV115	0·0016	0·048	0·35	115	118	119
KAV 79	0·0020	0·038	107	119	106	KAV113	0·0022	0·040	0·35	113	119	112
KAV 81	0·0025	0·050	107	118	114	KAV123	0·0027	0·043	0·36	113	119	94
KAV 83	0·0030	0·045	109	119	42	KAV125	0·0031	0·049	0·34	116	119	116
KAV107	0·0035	0·042	106	115	46	KAV127	0·0035	0·043	0·33	108	101	72
KAV 89	0·0040	0·026	107	119	116	KAV129	0·0040	0·045	0·36	114	82	63
KAV 91	0·0051	0·039	109	119	37	KAV131	0·0051	0·044	0·37	112	106	73
KAV 93	0·0060	0·040	108	118	24	KAV133	0·0062	0·043	0·39	109	64	67
KAV101	0·0074	0·042	114	32	21	KAV135	0·0075	0·044	0·38	107	87	107
KAV103	0·010	0·035	105	110	18	KAV137	0·0092	0·043	0·41	41	61	78

Values above and below about 95 ft.lb. were respectively partially broken and broken.
* No bismuth addition.

TABLE VII.—*Bismuth Transfer in Thin Copper Under Bright-Annealing Conditions. (Recipient Separated from Donors by a 2-mm. Gap. Each Recipient with its Two Donors Wrapped Separately in Copper Foil.) Annealing Treatment:* 1 *hr. at* 600° *C., Followed by Quenching.*

Donor.					Recipient.					
Mark.	Original Composition, %.			Bi after test, %.	Mark.	Original Composition, %.			Bi after test, %.	Drop in Reverse-Bend Value.
	As	P	Bi			As	P	Bi		
KAV 103	...	0·035	0·010	0·0088	KAV 71	...	0·046	0·00005	0·0014	From 44 to 24.
					KAV 121	0·36	0·040	0·0001	0·0009	From 38 to 28.
KAV 137	0·41	0·043	0·0092	0·0090	KAV 71	...	0·046	0·00005	0·0015	From 43 to 21.
					KAV 121	0·36	0·040	0·0001	0·0013	From 39 to 23.

Relatively thick pieces of copper of different bismuth content annealed in air showed no transfer effects. Arsenical and non-arsenical notched-bar specimens of deoxidized coppers containing 0·005% bismuth showed no change in their test values after annealing while stacked between, and completely surrounded by, similar specimens containing 0·01% bismuth.

VII.—SUMMARY AND CONCLUSIONS.

The practical aspects of bismuth embrittlement of deoxidized coppers have been studied by laboratory rolling trials and by the manufacture on an industrial scale of tubes and strips. In the main, the behaviour of the coppers was consistently related to their bismuth contents. Arsenical and non-arsenical coppers behaved somewhat differently, both in working operations and in laboratory tests, but the differences were minor and were not altogether consistent; in some cases the non-arsenical materials were slightly less affected by the presence of bismuth while in others the reverse was true. For practical purposes it is concluded that arsenical and non-arsenical deoxidized coppers are similarly affected by a given bismuth content, and hereafter no distinction is drawn between these two materials. Where tolerance limits for bismuth are quoted in the following conclusions, the lower figure has been taken when the two coppers behaved differently.

The grain-size of the materials has been shown [1] to affect markedly the degree of bismuth embrittlement, so that values for grain-size are

an essential part of their description. The following conclusions refer to the materials used in the present investigation, with grain-sizes in the range 0·02–0·07 mm. $\sqrt{\text{area}}$; the approximate values varied with the temperature of heat-treatment, i.e. 550° C., 0·02 mm.; 650° C., 0·04 mm.; 750° C., 0·07 mm.

The principal conclusion drawn from this work is that modification of annealing practice on the lines indicated by present knowledge of the mechanism of bismuth embrittlement raises the limiting bismuth contents beyond those at which failures may occur using normal methods of fabrication. Notably, a relatively high intermediate annealing temperature, followed by quenching, permits successful cold working of materials which would otherwise fail.

Detailed conclusions are as follows:

1. *Hot Working.*

(*a*) Hot rolling at 820° C. or higher is practicable with up to and including 0·03% bismuth; higher bismuth contents cause cracking. At lower rolling temperatures, severe cracking occurs with lower bismuth contents, e.g. 0·015% at 550° C. and 0·005% at 500° C.

(*b*) Hot piercing is satisfactory at 900° C. with bismuth contents up to and including 0·0075%, and only slight (tolerable) cracking occurs with 0·01% bismuth.

(*c*) Hot bending at 550° C. is satisfactory with bismuth contents up to and including 0·0025%. From analogy with the cold-working behaviour of annealed and quenched material, it is likely that higher bismuth contents would be tolerable in bending at higher temperatures, e.g. 0·005% at 700° C. and 0·007% at 750° C.

2. *Cold Working.*

(*a*) Cold rolling of chill-cast materials is satisfactory with up to and including 0·01% bismuth; higher bismuth contents cause slight edge cracking, but annealing and quenching from 900° C. raises the permissible limit to approximately 0·03%. The cold-rolling properties are thus relatively insensitive to bismuth content, and it is likely that bismuth limits for practical purposes will be determined by considerations other than rolling behaviour.

(*b*) Tube drawing and the associated severe tagging operations are satisfactory with bismuth contents up to and including 0·0075%, provided that the materials are annealed at and quenched from 750° C., both before working and at intermediate stages. Materials annealed at and quenched from 650° C. behave satisfactorily with up to and

including 0·0025% bismuth, and the same limit applies for materials annealed at 550° and 600° C.

(*c*) Judging by the behaviour in flattening and doubling-over tests, material annealed at and quenched from high temperatures during manufacture will be re-embrittled if after further cold work it is subsequently annealed at and quenched from lower temperatures.

(*d*) Cold bending of "quarter-hard" tubes, annealed at 550° C. during processing, presents no difficulty with bismuth contents up to and including 0·003%, and it is likely that considerations of tube-drawing behaviour rather than of cold-bending behaviour will fix the tolerance limits for materials destined for tubes.

3. *Annealing Procedure.*

(*a*) Oxidizing annealing atmospheres reduce bismuth embrittlement to some extent in relatively thin-section materials, e.g. 0·03 in. thick, but the effect is not large and is unlikely to be of practical use in view of the obvious objection to such treatment of thin material.

(*b*) Rapid cooling after annealing is essential if the benefit of high-temperature annealing is to be fully realized, and quenching is necessary unless the material is of sufficiently thin gauge to cool rapidly in air.

(*c*) Bismuth transfer can occur to coppers of thin section (e.g. 0·03 in. thickness) from closely adjacent copper of higher bismuth content when annealing is carried out in bright-annealing atmospheres. This possibility should be borne in mind, although there is no evidence that it is of practical significance under industrial conditions and with the bismuth contents normally encountered.

VIII.—Practical Recommendations.

1. *Hot Working.*

Severe hot work should not be performed in the temperature range 400°–700° C. with bismuth contents of 0·002% or more. Relatively mild work is practicable in this temperature range with contents up to and including 0·003%. Temperatures appreciably above this range, e.g. 750°–900° C., are recommended for materials of higher bismuth content, or where the working operation is severe.

2. *Cold Working.*

Cold work should be preceded by annealing at relatively high temperatures and quenching, the annealing temperature required varying with the bismuth content of the copper and the severity of the

working operation. For example, severe cold work should be preceded by annealing at and quenching from :

650° C. for material containing up to 0·0025% bismuth.
750° C. „ „ „ from 0·0025 to 0·007% bismuth.

Temperatures about 50° C. lower are permissible if only mild cold working is to follow.

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The work represents part of a general investigation of the effects of bismuth, selenium, and tellurium in copper.

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THE PROMOTION AND ACCELERATION OF METALLIC CORROSION BY MICRO-ORGANISMS.*

1140

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(Communication from the British Non-Ferrous Metals Research Association.)

SYNOPSIS.

During recent years many corrosion investigators have had good reason to suspect that micro-organisms can play a part in the corrosion of metals.

In 1936 the British Non-Ferrous Metals Research Association began research on the influence of bacteria and other living organisms, in the corrosion of condenser-tube alloys.

This paper gives details of some of the more important of these researches, and describes experiments devised to show that bacteria are able to initiate and accelerate corrosion. This can occur both by direct attack, during the life of a bacterial colony closely associated with a metal surface, and by indirect attack due to the accelerative corrosive action of some products of bacterial metabolism. In the latter case, acceleration of a corrosion cell may be effected at some distance from the site of the bacterial activity, and can occur under sterile conditions if certain products, produced during the bacterial breakdown of protein, are still present.

I.—INTRODUCTION.

OF recent years, many of those who have investigated the problem of metallic corrosion have had reason to suspect that bacteria, moulds, and other living organisms can play a part in such action.[5, 14, 20, 21, 29, 45]

The suggestion that bacteria might have an influence in the corrosion of metals was made by Garrett as early as 1891.[18] In discussing the increase in the corrosive action of water on lead, caused by compounds of nitrogen, Garrett suggested that under some conditions the ammonia content of a water might be increased through the bacterial breakdown of organic matter, and that bacteria might also be responsible for the oxidation of the ammonia to nitrite or nitrate, thereby making the water more aggressive. More modern investigation along the same lines has been reported by Hill [27] and Caldwell and Ackerman [11] in 1946. In 1921, Grant, Bate, and Myers [19] brought forward evidence to show that the rate of pitting of condenser tubes in

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a power station using cooling water from Sydney Harbour was seriously increased by ammonia produced in the shut-down condensers by bacterial action on the organic matter in the stagnant cooling water contaminated with sewage. Bengough and May [3] also found that some condenser-tube failures were associated with the products of micro-biological action. In 1923 von Wolzogen Kühr and van der Vlugt [46, 47] called attention to the effect of the sulphate-reducing bacteria on the corrosion of iron pipe-lines, a subject which has received considerable further study at the hands of Baars,[1] Bunker,[6–10] Hadley, [22, 23] Starkey,[41] and many others,[17, 42, 44, 48, 51] while Rogers [37, 38] has studied these bacteria in relation to other metals.

Although modern corrosion literature contains references to the effect of bacteria in causing corrosion of metals, very little experimental laboratory work, other than with sulphate-reducers, seems to have been undertaken. In 1936 the British Non-Ferrous Metals Research Association initiated research on the influence of micro-organisms in the corrosion of condenser-tube alloys, and since then many cases have been noted of their influence in the corrosion of metals. The sulphate-reducing organisms have been found to be responsible for accelerated attack on non-ferrous materials as well as iron. In some cases, organisms other than bacteria have been found to influence corrosion, e.g. moulds developing during corrosion tests can have very disturbing effects, and acid exudates from lichens have been found to increase corrosion of outdoor metallic structures.

Corrosion by bacterial action can be brought about in various ways : (*a*) by direct action, e.g. by the production of corrosive substances such as carbon dioxide,[39] hydrogen sulphide, ammonia,[27] organic or inorganic acids [2, 27, 50] ; (*b*) by the metabolism of the bacteria, producing organic products which can act as depolarizers or catalysts of corrosion reactions ; and (*c*) in cases similar to the anærobic corrosion of iron, by the activities of the sulphate-reducing organisms, where under some conditions the corrosion reaction is an integral part of the metabolic cycle of the bacteria. These divisions are arbitrary, and overlapping must be expected to occur, but they are used here for convenience in presenting the work.

Colonies of bacteria producing substances under (*a*) may be in close contact with the metal surface, growing in almost stationary slimy deposits, and in this case the necessary concentration of corroding agent is often maintained only in the locality of the colony, and may be undetectable in the surrounding water or soil. Bacteria causing corrosion in this way, need only produce very small quantities of a corrosive product for localized attack to become very severe. More-

over, the colony, although not producing any markedly corrosive substance, may act as a deposit, so setting up a differential oxygen cell or causing an unequal distribution of electrical potential, giving rise to local anodes and cathodes.

In other conditions the corroding medium may be generally infected with the offending organisms, and if they produce substances which are able to catalyse corrosion reactions, it is possible for the medium to remain abnormally corrosive even after the bacteria have died, become dormant, or been removed.

This paper describes many experiments, using pure and mixed cultures of bacteria isolated from contaminated waters, both fresh and marine, which show that under some conditions colonies of certain bacteria can considerably increase the corrosive attack on metals. It also shows that substances known to be produced by bacterial metabolism can cause accelerated corrosion.

II.—Local Corrosion Caused by Bacteria.

1. *Experimental Methods.*

Several waters were examined bacteriologically, and cultures of bacteria obtained therefrom; these included samples of sea waters which had caused abnormal pitting of condenser-tube alloys in laboratory impingement tests,* water from an inland power station using sewage effluent for cooling, and estuarine water from a coastal power station. These bacteria, in both mixed and pure cultures, were used in corrosion tests.

A suitable test for the corrosive action of bacteria must comply with both corrosion and bacteriological requirements, and a technique had to be developed for maintaining active colonies for long periods in stationary slimy deposits on the surfaces of metal tubes or specimens. The method used by Grant, Bate, and Myers [19] did not prove satisfactory for long-period tests, and a new technique was developed which (*a*) enabled the bacterial colony to be fed and maintained in close contact with the metal, and (*b*) prevented desiccation of the colonies even over long periods. A flat circle of agar 1 in. in diameter by $\frac{1}{4}$ in. deep was cut into two semi-circular halves and the two halves set in a petri dish about $\frac{1}{4}$ in. apart. The tops of these half circles were inoculated with selected bacteria and used as a base for the colonies. A small specimen of the metal to be tested was placed on top of these semi-circles of agar after the colonies had been allowed to develop for 24 to 48 hr., and the

* The assessment of condenser-tube alloys for service is usually carried out in the jet impingement apparatus developed by R. May.[31]

petri dish filled with sufficient liquid * to cover the agar and the test-piece. By this means contact between the metal and the colony was effected; the division between the half circles giving free access to water and air, toxic salts could diffuse out, and the fluid could be pipetted off and replaced under sterile conditions as required.

2. *Copper Tolerance.*

Early work showed that colonies of some bacteria and also moulds growing in contact with 70 : 30 brass were able to accelerate corrosion and cause deep pits underneath the colonies. Results were variable, and many colonies quickly died out, which was not surprising as copper salts, the normal corrosion products of brass, are usually toxic to bacterial growth. That some bacteria could tolerate a high concentration of copper salts was obvious, as organic matter was present within many of the pits.

This factor is especially important in stagnant conditions, but may not be so significant where the corrosion products are being washed away by flowing water. It was found that many of the cultures isolated from an estuarine water showing abnormal corrosion properties could withstand concentrations of copper salts much higher than that usually stated in the literature to be lethal to micro-organisms. Several of the non-sporing types isolated could withstand concentrations of copper higher than 100 p.p.m. One of these was a non-sporing, Gram negative rod, forming a reddish-brown colony, and appeared to be a similar organism to that isolated from sea water by Waksman *et al.*[48] The suggestion of these workers that copper was necessary for normal development of this bacterium was not tested as the organism was isolated from copper-containing water and then cultured into copper-containing sea-water medium. Another culture, a spore-forming organism, taken from a metal specimen corroding in infected sea water, resisted 2000 p.p.m. of copper. All the cultures taken from the jet impingement apparatus have been found capable of withstanding a higher copper concentration than that normally accumulating in waters during tests with this apparatus.

3. *Increase of Corrosion Due to Bacterial Activity.*

The series of cultures isolated from estuarine water known to be corrosive, and also a culture obtained from the pitted area of a piece of metal corroding in sea water in the jet impingement apparatus, were tested by the technique mentioned above. The fluid used for

* Sterile water with and without added nutrients.

flooding the petri dishes was sterile sea water and the test metal 70 : 30 brass. It was found that in many cases appreciable corrosion took place underneath the colonies in as short a time as 28 days. The type of corrosion obtained was more rapid than that associated with normal deposit attack and was often intercrystalline. The controls showed no more attack than is normally found with 70 : 30 brass in sea water.

Efforts were made to increase the rate of attack due to the bacteria by adding to the sea water substances which would act as foodstuffs for them and so increase their activity. Earlier work had suggested that organic acids produced as a result of the breakdown of sugars have an influence on corrosion in sea water, and in one series of experiments mannitol together with asparagine, as a source of nitrogen, were added to the sea water. The specimens showed severe attack, the measured depth of the pits being from two to ten times as great as that obtained in the previous tests. Some of the specimens showed a protective film, but it had often been broken down, and in these cases attack had continued underneath the film, which flaked off when touched with a needle, revealing a deep pit. The fact that the addition of mannitol to sea water made such a great difference to the magnitude of the attack is of interest because mannitol is a constituent of many seaweeds,[28, 34, 43] and although its presence in the open sea is doubtful, it is highly probable that estuarine waters will at times contain this substance and also that inshore water will contain organic acids or their salts derived from its breakdown.

In another series, in which peptone was added to the sea water, it was found that the peptone favoured film formation on the metal. Some bacteria were able to break down these films, while others were unable to do so. It was found that some colonies which were unable to break down the protective film and pit the metal did so if the surface film was broken by scratching.

Further work was undertaken using the same technique with pure (single strain) and impure (mixed strain) cultures, and it was found that impure cultures always produced the more severe attack.

In practice the influence of bacteria on corrosion usually occurs in conditions of flowing water, and it was thought that changing the liquid during the tests would accelerate attack, by removing from the solution some of the copper salts which, even if not toxic, interfere with film formation on the metal. Tests were therefore made in which the liquid was changed during the course of the experiment. The first change was made three days after inoculation and the second after a further seven days; the test was then left until the full 28 days had elapsed before examination was made. The results taken as a

whole showed quite clearly that changing the liquid increased the corrosion.

Samples of water have been taken from the jet impingement apparatus and estimates made of the bacterial numbers. These counts have shown that the sea-water samples received into the laboratory vary greatly in bacterial population and in the type of bacteria present; nor does the bacterial population remain constant during storage.[24] It has also been shown that the bacterial population of the jet impingement apparatus will vary during a run. The work suggested that a high bacterial count does not necessarily imply that the water will be exceptionally corrosive, but that the presence in the water of bacteria forming viscid or slimy colonies will usually be associated with anomalous results in corrosion tests.

It was shown that many of the bacteria found in the sea waters used in jet tests could be inhibited by the use of the dye Gentian Violet. Addition of this dye to sea waters used for jet-test runs controlled most forms of bacterial attack, but occasionally abnormal results were obtained which were attributed to a resistant strain of bacteria developing preferentially in the presence of this dye.

These experiments showed that bacteria are capable of having an effect in corrosion by sea water. How the bacteria accelerate corrosion was not immediately obvious, but the work has made certain suggestions possible. The present author's theory is that the acceleration of corrosion by bacteria, under these conditions, is mainly due to the presence of hydrogen acceptors and oxidation–reduction systems set up during bacterial metabolism. It is suggested that the presence of mannitol accelerates corrosion because, during its fermentation by the bacteria, hydrogen acceptors capable of causing depolarization are produced. That the bacteria used in these experiments did contain enzymes capable of both activating hydrogen and catalysing dehydrogenation reactions was proved by experiment, using the Thunberg tube technique.[12]

4. *Effect of Moulds.*

A few investigations were made on the corrosive action of moulds. When the moulds were grown on gelatine on the surface of brass plates, deep pits were rapidly and regularly produced by the common moulds of the atmosphere. In this case the attack was most probably caused by the diffusion to the metal of the organic acids known to be produced during the growth of many moulds.

Many bacteriological examinations have been carried out concurrently with runs of the jet impingement apparatus. Several times

it has been shown that severe corrosion is associated with infections of bacteria and moulds of a type which will cause attack when tested experimentally under stagnant conditions.

III.—Corrosion Caused by General Bacterial Infection.

1. *Pigments.*

Work on condenser-tube corrosion at the British Non-Ferrous Metals Research Association has often revealed cases in which failure due to abnormally rapid pitting appeared to be connected with some variable property of sea water not revealed by ordinary chemical analyses, and of more or less seasonal incidence. It was noticed that this rapid pitting tended to occur when the surface of the metal was coated with a brown film, which examination suggested was of biological origin. This view received some confirmation from the work on corrosion by colonies of bacteria, where it was noticed that some which produced black or brown pigments were among those causing the most severe corrosion.

One pigment was found to be melanin, an organic substance produced by the action of the enzyme tyrosinase on tyrosine, and it was shown that bacteria producing tyrosinase could accelerate corrosion in direct relation to the amount of tyrosine present. Acceleration of corrosion may be brought about in this case by the formation of quinones during the fermentation reaction, which may possibly play a part in cathodic depolarization.

2. *Sulphur Compounds.*

Samples of sea water known to give rapid pitting were also found to contain an organic sulphur compound, capable of being repeatedly reduced to a mercaptan and oxidized back to a disulphide. As these changes could be brought about readily, it appeared possible that the compound, when present on the metal surface, might act as an oxygen carrier, speeding up the depolarization of the cathodic areas around the pits, thereby increasing the rate of pitting. It was also noticed that sometimes a sample of sea water which gave no pitting did so if it became "infected" with a very small quantity of a water which had these properties. This again suggested that bacteria might be responsible, and as some of the bacteria isolated in the static tests gave positive nitroprusside * reactions for sulphydryl groups, considerable attention was paid to these substances.

* To determine the presence of –SS– and –SH groups, extensive use was made of the nitroprusside test. This test was devised by Mörner [33] and depends on the fact that sodium nitroprusside, in alkaline solution, produces a deep purple coloration in the presence of soluble sulphides and –SH groups. –SS– groups give the colour after reduction with *sulphide-free* KCN.

The principal sulphur compounds entering into protein structure are the disulphide, cystine * (CSSC), and its corresponding mercaptan form, cysteine * (CSH), also a similar substance, glutathione * (a stable complex of the three amino-acids, cystine, glycine, and glutamic, which, like cystine, exists in disulphide * and mercaptan forms), and methionine.*

Sulphydryl compounds are capable, under certain conditions, of reversible oxidation–reduction reactions. Thus cysteine in alkaline solution, in the presence of oxygen and traces of various catalytic metals, is oxidized to cystine. Copper is one of these metals, and it is effective in extremely small concentrations.[30, 40] After oxidation the cystine can be reduced again by reducing agents such as active hydrogen or sulphites.

Glutathione is also capable of similar behaviour in the presence of a metal catalyst, but methionine, since it contains no –SH group, does not give rise to any oxidation–reduction system.

The source of these compounds is plant and animal tissue. Glutathione is present in all tissues, cystine in many, and both can be released by bacterial action. Many seaweeds contain cystine, and in the *Laminariae*[32] there may be as much as 3·4%. Cystine may possibly diffuse from the living plant, but when the weed decays through bacterial action, it is certainly liberated into the surrounding water, and this was confirmed by experiment. Some *Laminaria* was allowed to decompose in the laboratory, and cystine was detectable both in the water and in the bacterial slime on the decomposing weed.

As cystine, glutathione, and methionine are all of protein origin, and as bacteria are the active agents in protein decomposition, it may be safely argued that the presence of these compounds in sea water is

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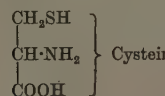
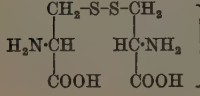
* Cysteine (CSH): β-thio-α-aminopropionic acid.
Cystine (CSSC): di-β-thio-α-aminopropionic acid.
Reduced glutathione (GSH): glutamyl-cysteinyl-glycine.
Oxidized glutathione (GSSG): di-glutamyl-cysteinyl-glycine.
Methionine: γ-methylthiol-α-aminobutyric acid.
Formulæ:



Cysteine.



Cystine.

due to the action of micro-organisms in releasing them from decomposing organic matter.

Harvey [25] has shown that compounds such as cystine and glutathione are found in both off-shore and in-shore waters, and that there are definite seasonal variations in the amounts present. Also these substances are present in greater quantity where organic matter is being broken down, such as in estuaries, harbours, &c.

It is well known that the corrosion of metals is governed mainly by the type of film which forms on the surface of the material and the presence or absence at the seat of corrosion of substances which can behave as anodic or cathodic depolarizers. One of the main characteristics of cystine from the corrosion viewpoint is its affinity for certain metals and its ability to form metallic complexes on their surfaces. As has already been stated, cystine and its reduced form cysteine are capable of forming a reversible oxidation–reduction system of the type [26]:

$$\underset{\text{(disulphide)}}{\text{Cystine}} \quad \underset{\text{Cys-SS-Cys} + 2\text{H} + 2\text{e}}{} \quad \rightleftharpoons \quad \underset{\text{2 Cys-SH}}{\underset{\text{(mercaptan)}}{\text{Cysteine}}}$$

This suggests that the system might well cause depolarization at a corrosion centre. Thus cystine would appear to have two characteristics which under suitable conditions could have considerable influence on corrosion, namely the property of forming films and a depolarizing action.

The effect of these substances in the acceleration of corrosion, and the importance of organic sulphur compounds of the mercaptan–disulphide type in accelerating the corrosion of copper and copper-base alloys, are shown in Section IV.

IV.—Cystine as an Accelerator of Corrosion in Sea Water.

1. *Acceleration of Impingement Attack.*

To prove that a mercaptan–disulphide system was an effective corrosion accelerator, experiments were carried out under sterile conditions on 70 : 30 brass and other standard condenser-tube materials, in sea water with and without additions of cystine and glutathione.

As the jet impingement apparatus,[31] in which several specimens undergoing impingement are tested together in one large container, does not lend itself to sterile conditions, the Brownsdon and Bannister impingement corrosion apparatus,[4] which uses a separate unit for each test, was modified for the purpose. To find the normal rate of attack for each jet in the absence of organic sulphur, 12 control 70 : 30 non-

arsenical brass specimens were first tested in a run of 500 hr. under sterile conditions, in a sea water that gave a negative reaction to the nitroprusside test and to Feigl's mercury-bead test,[15] and showed no abnormal pitting action. Sterile air was fed to the jets, and frequent checks showed that the apparatus remained sterile under working conditions.

Several runs were then made using the same jets in sea water from the same batch, sterilized and with the addition of varying amounts of the sulphur compounds, the breakdown of which was prevented by the sterility of the apparatus. In case sterilization of the sea water by heat in an autoclave had affected its corrosion properties, a few tests were made using the sea water which had not been autoclaved. A test was also made in the presence of cystine in water which had been infected with a culture of bacteria isolated from a sample of sea water producing abnormal attack.

All the specimens which had been tested in waters containing sulphur compounds were found at the end of the runs to have developed brown films to a varying extent. These films closely resembled the film often found in cases of abnormally rapid pitting in practice. Also, the presence of the sulphur compounds vastly increased the amount of pitting as compared with controls run in water free from these substances as shown by the tests quoted above.

A selection of the results obtained is given in Table I. Some of the tests were repeated several times, and to ensure that the pitting was not due to the peculiarity of a particular jet, similar experiments were made using different jets. The results were substantially the same.

The work established that when these substances were present, corrosion was accelerated even under sterile conditions. There is evidence, however, that if certain bacteria are in the water the rate of corrosion may be increased still further (Table I, jet No. 2*a*).

2. *Effect on Impingement Attack of the Decontamination of Sea Water.*

Before the effect of cystine as a corrosion accelerator could be correctly assessed, however, it was necessary to obtain a decontaminated water either free from, or containing only a very small quantity of, cystine and related compounds. Thus, sea waters to which sufficient cystine had been added (about 50 mg./l.) to give a bright nitroprusside reaction, were treated with the following substances: activated and granulated charcoal, metallic copper, cupric oxide, cuprous chloride, chlorine, bromine, and hydrogen peroxide.

TABLE I.—*The Effect of Organic Sulphur Compounds as Corrosion Accelerators on Non-Arsenical* 70 : 30 *Brass.*

Jet. No.	Sulphur Compound Added (parts per 100,000).*		Depth of Pit, mm.		Remarks.
			Control.†	Test.	
3*a*	3·3	Cystine (sterile)	0·07	0·43	Severe impingement attack, concentrated over an area which had progressively decreased in size by the encroachment of a thin brown cathodic film. Thick brown film also present on the anodic area.
5*a*	3·3	Cystine (non-sterile)	0·06	0·41	Severe impingement attack, gradually increasing in area. Brown film was less pure than in 3*a* and was being gradually removed as attack spread. Some brown film over anodic area.
1*a*	2·5	Cystine (sterile)	0·02	0·36	Closely resembling 3*a*.
2*b*	1·0	Cystine (sterile)	0·06	0·30	Same, but cathodic film thinner; anodic film thin and apparently continuous over centre of attacked area.
4*c*	0·1	Cystine (sterile)	0·05	0·39	Anodic film absent over attacked area. Cathodic film thin but strong and apparently very active, causing impingement attack to be more concentrated.
5*c*	0·01	Cystine (sterile)	0·06	0·23	No anodic brown film. Cathodic film weaker, and had not been able to prevent spreading of the attack.
6*c*	0·001	Cystine (sterile)	0·07	0·11	No anodic film and only a trace of cathodic film; attacked area had spread almost as much as controls.
3*b*	3·3	Reduced glutathione (sterile)	0·07	0·31	Severe impingement attack, gradually increasing in area by the undermining of a cathodic film. The undermining was associated with the development of pits close to the edge of the main area of attack.
6*b*	3·3	Reduced glutathione (non-sterile)	0·07	0·35	Resembled 3*b*, but the pitting and undermining of cathodic scale was less marked.
4*b*	0·1	Reduced glutathione (sterile)	0·05	0·39	Impingement attack localized by the cathodic film, which was being undermined by severe pitting under blisters around the main anodic area.
2*a*	3·3	Cystine (unsterile + culture *P/G*) ‡	0·06	0·55	General corrosion similar to 3*a* except that attack was deeper and larger. Film very thick.

* i.e. Weight in grammes per 100,000 c.c. of water.

† Sterile run without cystine additions.

‡ Culture *P/G* was isolated from an actively pitting brass specimen which had been in natural sea water.

The oxidants chlorine, bromine, and hydrogen peroxide decomposed the cystine and it was impossible to estimate the exact amount required. Charcoal was only partially successful in removing the cystine. It was troublesome to use, tended to colour the water, and possibly affected the carbonate equilibrium as well as removing scale-forming substances. Use of these reagents was not continued.

The copper compounds were quite successful; they precipitated the cystine, but in the absence of exact knowledge of the reaction between them and cystine, an excess had to be added, again an undesirable condition in corrosion experiments. The most suitable method appeared to be to pass the sea water over metallic copper; this is easy to carry out and does not contaminate the water with any undesirable amount of salt or reagent. A small amount of copper salt was, of course, introduced into the water, but this was found to be insignificant. Several jet impingement apparatus runs have been made using this method, and it has been found that a sea water so treated has reduced corrosive properties and does not deposit on the surface of the specimen the dark film which is often associated with abnormal corrosion behaviour.

It is well known that cystine has a great affinity for copper and copper salts, and the use of copper oxide for the extraction of cystine from protein hydrolysates is familiar, the organic sulphur compound being precipitated as a copper mercaptide complex.[36]

Several experiments have been made, both in the Brownsdon and Bannister impingement apparatus and in the May jet impingement apparatus, to compare the corrosion behaviour of alloys in contaminated and decontaminated waters. In general, it has been found that decontamination considerably lessens the severity of the corrosion, the amount of which increases again on the addition of cystine. It has also been shown that large amounts of cystine form films which stifle attack at the jet, but generally cause an increase in attack at areas shielded from oxygen, e.g. at blisters which tend to form in the film.

The important part which contamination can play in corrosion in sea waters is illustrated in Tables II and III. Removal, by activated charcoal, of most of the contamination of a natural water considerably reduced attack at the jet and at " shielded areas ". The addition of extra cystine over and above the contamination already present in the natural sea water, stifled attack at the jet owing to the formation of heavy films, but attack at the " shielded areas " became increasingly severe. In 3% sodium chloride no attack occurred at the jet or at " shielded areas ", but the addition of 10 mg./l. cystine to this solution caused attack of the type observed in natural sea waters (Fig. 1, Plate I).

TABLE II.—*Copper–Nickel–Iron Alloy Containing* 5% *Nickel and* 5% *Iron Tested in the Quenched and Cold-Rolled Condition in the Brownsdon and Bannister Apparatus Under Varying Conditions of Contamination* (*see Fig.* 1, *Plate* I).

Specimen.	Water.	Depth of Attack at the Jet, mm.	Remarks.
A/1	Natural, dirty.	0·35	Deep attack at the jet, some attack at "shielded areas".
A/2	Natural, dirty.	0·89	Deep attack at the jet, some attack at "shielded areas".
A/3	Natural, as above, cleaned activated charcoal.	0·12	Attack at the jet, no attack at "shielded areas".
A/4	Natural, as above, cleaned activated charcoal.	0·11	Attack at the jet, no attack at "shielded areas".
A/5	Natural, as above, plus 35 mg./l. cystine.	Nil	Heavy film, attack at the jet stifled. Very severe attack at "shielded areas" and some blistering.
A/6	3% NaCl in distilled water.	Nil	No attack at "shielded areas" or at the jet.
A/7	As above, plus 10 mg./l. cystine.	0·16	Attack at the jet and at "shielded areas".

TABLE III.—*Copper–Nickel–Iron Alloy Containing* 5% *Nickel and* 5% *Iron Tested in the Aged* 600° C. *Condition in the Brownsdon and Bannister Apparatus, Using Contaminated and Uncontaminated Sea Waters* (*see Fig.* 2, *Plate* I).

Specimen.	Water.	Cystine Additions.	Depth of Attack at Jet, mm.
A	Clean natural sea water	None	0·01
B		Plus 0·5 mg./l. cystine	0·20
C		Plus 2·0 mg./l. cystine	0·38
D	Partially decontaminated dirty sea water	None	0·23
E		Plus 0·5 mg./l. cystine	0·52
F		Plus 2·0 mg./l. cystine	0·54

Two different waters, one a clean sea water, and the other a sea water partially decontaminated by passage over copper, were used

with and without added cystine (Table III). In each case the addition of cystine increased the corrosion (see Fig. 2, Plate I).

3. *The Effect of Cystine on the Corrosion of Copper.*

The effect of cystine on the corrosion of copper was studied by immersing sheets of high-conductivity copper, 1 dm.^{2} in area, in beakers containing 600 ml. of sea water, with and without added cystine. The liquid was stirred by a jet of air which was not allowed to impinge upon the metal, and the water changed every 48 hr. The corrosion of the copper was in each case measured by chemical estimation of the total copper salts in the beakers. Fig. 4 (Plate II) shows the results of these experiments in clean sea water and in sea waters containing respectively 3, 25, and 50 mg./l. cystine. The curves were obtained over a period of three weeks. All points on the graphs are the average of not less than four experiments, with the exception of the last three points of the 50 mg./l. experiments, which were obtained respectively from three, two, and one experiments.

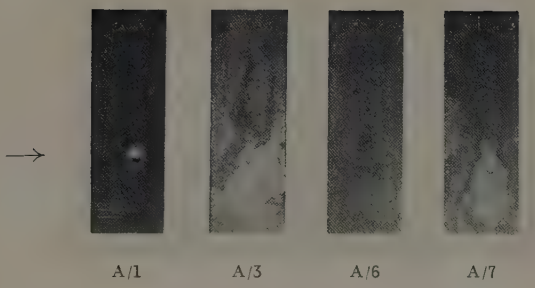
It will be noticed that curve *A*, no added cystine, departs from a straight line only by showing a slight alteration in slope at about 10 days. This increase in rate at about this period was found to occur in all the experiments and seemed to be associated with the development on the copper specimens of a patchy light-brown film. Whether this was caused by the cumulative film formation due to small quantities of cystine present in the natural sea water is not known.

In all cases the corrosion of copper is initially increased by the presence of cystine. In the case of sea water to which 3 mg./l. cystine has been added (curve *B*), the accelerated rate compared with that in sea water containing no added cystine (curve *A*) continues until the tenth day, while in waters with higher concentrations of added cystine (curves *C* and *D*), the accelerated rate persists for only two days and then begins to fall off.

In each of the three series of experiments made in sea water containing added cystine, it was found that, after varying periods of time depending on the concentration of cystine, the corrosion rate slowed down until it was less than in water containing no added cystine, but none of the cystine concentrations used produced a film which was completely protective.

Copper corroding in the presence of cystine becomes brown, owing to the formation of a film of cystine–copper complex, which gives a positive nitroprusside reaction. The film becomes darker as the amount of this complex increases.

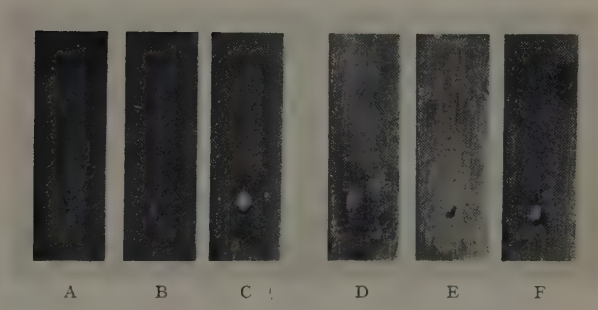
Some of the experiments with cystine suggested that it was possible



A/1 A/3 A/6 A/7

FIG. 1.—Specimens as Described in Table II, Showing Attack at the Jet Area in the Brownsdon and Bannister Apparatus. × 1.

A/1 Natural dirty sea water.
A/3 Natural dirty sea water cleaned through activated charcoal.
A/6 3% NaCl in distilled water.
A/7 3% NaCl in distilled water plus 10 mg./l. cystine.



A B C D E F

FIG. 2.—Specimens as Described in Table III, Showing Attack at the Jet Area in the Brownsdon and Bannister Apparatus. × 1.

A. No cystine, clean natural sea water.
B. As A, plus 0·5 mg./l. cystine.
C. As A, plus 2·0 mg./l. cystine.
D. Partially decontaminated dirty sea water.
E. As D, plus 0·5 mg./l. cystine.
F. As D, plus 2·0 mg./l. cystine.

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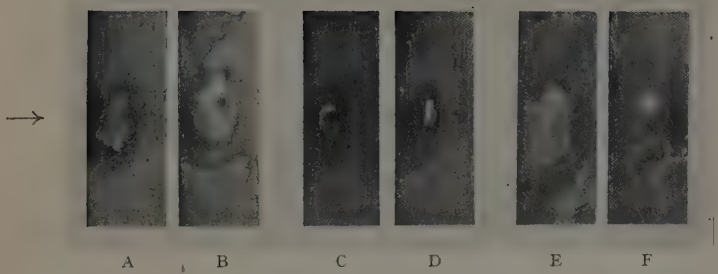

FIG. 3.—Specimens as Described in Table IV, Showing Attack at the Jet Area in the Brownsdon and Bannister Apparatus. × 1.

A and B. 48 hr. exposure to cystine-containing sea water before test.
C and D. 240 hr. exposure to cystine-containing sea water before test.
E and F. No exposure.

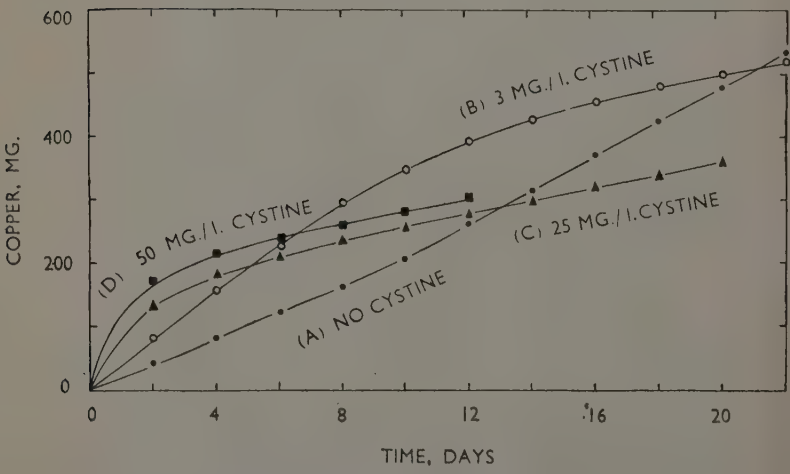

FIG. 4.—Curves of Total Copper *versus* Time. 1 dm.² H.C. copper in aerated sea water containing varying amounts of cystine. Water changed every 48 hr.

to obtain two forms of cystine film: incomplete films which may accelerate general corrosion, and more nearly complete films which tend to be protective but which can also accelerate pitting action.

If a copper sample is exposed to sea water containing a low concentration of cystine, filming of the surface is incomplete, and stimulation of attack is maintained even after all the cystine has been removed from the water. This is due to the fact that cystine first comes down preferentially on local anodes or cathodes (depending on the *p*H of the solution), and complete filming does not occur until all local preferences are satisfied. Further, if such a partially filmed specimen is transferred to a water free from cystine, acceleration of attack continues.

The effect of impingement on cystine films was studied by placing

TABLE IV.—*Impingement Experiments in Clean Sea Water on H.C. Copper Previously Exposed to Sea Water Containing* 25 *mg./l. Cystine* (*see Fig.* 3, *Plate* II).

Specimen.	Prior Exposure in Cystine-Containing Sea Water, hr.	Depth of Attack at Jet, mm.	Size of Unfilmed Area at Jet, cm.^{2}	Copper in Water at End of Experiment, mg./l.
A	48	0·18	0·50	78
B	48	0·15	0·55	79
C	240	0·30	0·10	53
D	240	0·27	0·08	51
E	None	0·05	No film	52
F	None	0·05	No film	72

Note.—In Specimens *A* and *B* the films at the jet broke down within a few hours, and by 100 hr. the whole jet area was bright. At the end of the run the original film was only present under the holder, the remainder having partially disappeared. There were distinct signs of localized attack all over the specimen where the film had become incomplete.

In *C* and *D* after 24 hr. both specimens had a bright area at the jet which attained its maximum area in a few days. At the end of the run both specimens were still well filmed except for the small area at the jet, to which corrosion appeared to be entirely confined.

In *E* and *F* there was general attack all over the specimens.

two copper specimens in sea water containing 25 mg./l. cystine for 48 hr. and two specimens for 240 hr., the sea water containing cystine being aerated and changed every 48 hr. These specimens, together with two unfilmed copper controls, were then tested in sea water containing no added cystine in the Brownsdon and Bannister apparatus for 500 hr. The results are shown in Table IV. The depth of attack at the jet, the size of the unfilmed areas, and the amount of copper salts in the flasks at the end of each separate run were measured.

In the experiment above, no filmed specimen had resisted attack at the jet for more than 24 hr., and the highly cathodic film on specimens *C* and *D* had concentrated the attack at the jet. The amount of copper in the water was considerably less in *C* and *D* than in *A* and *B*, suggesting that the thicker film, while concentrating attack at the jet, had had a definite protective effect over the rest of the specimen. These experiments show good examples of the two types of film which can be produced by cystine. Specimens *A* and *B* had a generally accelerative film all over their surfaces, while specimens *C* and *D* had thick films which were highly cathodic. The concentrated attack at the jet found on specimens *C* and *D* was an example of the acceleration usually found where mechanical breakdown occurs in a highly cathodic film (see Fig. 3, Plate II).

The reason for the discrepancy in the concentration of copper in solution for the checks is not understood, but corrosion was not confined to the jet, there being general attack all over the specimens.

Since the completion of these experiments on the effects of cystine as a corrosion accelerator of copper-base alloys, a routine examination has been made for the presence of organic sulphur compounds in all service failures sent to the British Non-Ferrous Metals Research Association for examination and report. In many failed tubes from marine condensers organic sulphur has been isolated from the areas o failure. In one case of repeated failure of condenser tubes at a foreign power station using estuarine cooling water contaminated with sewage, the black corrosion product on the tube walls was found to contain a copper–organic disulphide complex, and a violent form of pitting action had been caused by the presence of the organic sulphur.

V.—Other Instances of Micro-Organisms Causing Acceleration of Corrosion.

1. *Sulphate-Reducing Organisms.*

The action of these organisms in the anærobic corrosion of iron is well known and now has an extensive literature. With regard to non-ferrous metals, many cases of acceleration of corrosion owing to the presence of these organisms have been encountered, both in sea water and in fresh water. In the case of non-ferrous metals and alloys, corrosion does not necessarily take place during the activity of the sulphate-reducing organisms, the fact that hydrogen sulphide has been evolved being sufficient to bring about a violently corrosive environment, especially in sea water.

This property of hydrogen sulphide of rendering a sea water

abnormally corrosive once it has been evolved by bacterial action, is not entirely understood. It has been found both in laboratory tests and practical failures that sea water containing sulphate-reducing bacteria which have evolved hydrogen sulphide when the water has been stagnant, can remain extremely corrosive although conditions change to considerable aeration and no hydrogen sulphide is chemically detectable in the aerated sea water. The present author has investigated the inhibition of these sulphate-reducing organisms,[37, 38] and the use of dyestuffs of the diaminoacridine (flavine) types has been found very successful.[55]

2. *Slimes and Micro-Biological Deposits.*

The effect of bacteria and various micro-biological activities in causing fouling of ships' hulls received considerable attention during the war, and work reported in recent publications [52, 53, 54] has done much to clear up some doubtful points, such as the toxicity of copper and mercury salts to bio-fouling in general and the problems of leaching rate and succession of organisms. In condensers, both land and marine, the problem of bio-fouling can be extremely important, and much work has been done on the control of such growths.[13, 16, 35] As long as these slimes are alive their main effect is to reduce heat transfer, but when they die and decomposition sets in, corrosion troubles are likely to occur. Several well authenticated cases are known of condenser-tube failures in fighting ships being due to pitting, originally initiated by a mussel causing partial tube stoppage, aggravated by the decomposition of the mussel proteins, with the release of sulphur compounds.

3. *The Decomposition of Paraffin Wax.*

Many corrosion experiments are made using paraffin wax as a sealing agent or as a barrier between liquid and glass, but the present author has shown that bacteria can break it down to carbon dioxide and water, with consequent alteration in the *p*H of the corroding medium, thereby affecting corrosion experiments.[39]

VI.—Methods of Control.

Evidence that bacteria can play a part in the corrosion of metals has naturally led to investigation into methods of control. The most obvious method is to destroy the bacteria and so prevent their action. The problem of inhibiting the growth of bacteria under such conditions is difficult because many disinfectants have corrosive properties; also many disinfectants employed against pathogenic organisms, which

outside the human body have comparatively little resistance, are of no use against the true water forms unless used in much greater concentration than would be economic or desirable. When a survey is made of the substances which might fulfil the special requirements of this problem, non-corrosive dyestuffs should not be forgotten; in some cases of corrosion by bacteria it may be possible to find specific inhibiting dyes whose small effective concentration would be economic. It has been shown experimentally that a dye such as Gentian Violet can inhibit many types of the bacteria found in sea water which can interfere in corrosion experiments. Inhibition of the sulphate-reducing organisms in closed systems can be successfully carried out by the use of dyes of the diaminoacridine type, a method now being extensively used by some commercial undertakings where the activities of the sulphate-reducing bacteria are detrimental to their products.[38]

These methods are satisfactory when the amount of water is not too great and the system is closed, but in cases where the water is in circulation or where the amount to be treated exceeds the economic limit, the best way of combating bacterial corrosion is by the production of resistant alloys. It must also be pointed out that in many cases the bacterial production of corrosion accelerators occurs in natural waters long before they can be treated in any way, and this again calls for more resistant alloys rather than bactericides.

The use of chlorine in various dosages with and without ammonia is becoming increasingly popular in power-plant operation, and it must be borne in mind that chlorine, while excellent as a slime preventer, is not always a deterrent of indigenous water organisms, which are the ones most likely to cause a corrosive environment, and it may not destroy corrosion accelerators which have been released into a water by bacterial action before the water reached the chlorinating plant.

VII.—Conclusions.

Experiments have been described which show that bacteria, living in waters or other media in contact with metallic structures, can initiate or accelerate corrosion. Local attack can be increased if bacteria are present which produce substances, such as acids or alkalis, which, although insufficient to render a mass of liquid corrosive, can build up local concentrations of corrosive materials in the vicinity of a colony.

It has also been shown that products of bacterial metabolism, such as some organic sulphur compounds, can act as accelerators of pitting action; these substances are often very active in small concentrations

and when once released by bacterial action can cause a water to remain abnormally corrosive long after bacterial activity has ceased. It is thought that in some cases bacteria increase corrosion because in the course of their natural metabolism they produce or activate substances which can act as hydrogen acceptors or oxygen carriers, which in their turn affect reactions at the anodes and cathodes of corrosion cells.

Whatever may be the means by which micro-organisms affect corrosion, sufficient experimental work has been completed to show that the corrosive conditions of any environment cannot be assessed by physical and chemical methods alone. The biological aspect must also be taken into account.

Acknowledgements.

The author thanks the Director and Council of the British Non-Ferrous Metals Research Association for permission to publish the paper, and his colleagues in the Corrosion Department of the B.N.F.M.R.A for much helpful advice. Some of the work was done in the Bacteriological Department of the Imperial College, and the author records his appreciation of the help and facilities so freely given by Dr. S. E. Jacobs and his staff.

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THE CONSTITUTION OF ALUMINIUM-MAGNESIUM-ZINC-CHROMIUM ALLOYS AT 460° C.* 1141

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Synopsis.

The constitution of the aluminium-rich alloys of the system Al–Mg–Zn–Cr at 460° C. has been investigated, the maximum amounts of added materials being 20% of magnesium and 10% each of zinc and chromium. In the ternary system Al–Cr–Zn the $CrAl_7$ phase of the binary system Al–Cr can take up zinc into solid solution, and the resulting phase is a stable phase in most alloys containing more than small percentages of chromium. In the cast state many of these alloys contain crystals of the Cr_2Al_{11} phase surrounded by sheaths of $CrAl_7$, and annealing periods of the order of 2 months are required for the removal of the Cr_2Al_{11}. In the ternary system Al–Cr–Mg the stable phases in the alloys examined are $CrAl_7$ and a ternary phase of variable composition denoted *E*, and the same phases are found in quaternary alloys containing 2% and 8% zinc.

I.—Introduction.

Previous papers [1, 2, 3, 4, 5] have described the constitution of Al–Mg–Mn–Zn alloys at different temperatures, while the effect of 1% silicon on these alloys has also been studied.[6, 7] In order to understand the effect of chromium on this class of alloy, it is necessary first to determine the constitutional diagrams of the various quaternary systems which are involved, and the present paper describes an investigation of the constitution of Al–Mg–Zn–Cr alloys at 460° C., as determined by the microscopic examination of alloys after annealing at this temperature, the maximum amounts of added materials being 20% of magnesium and 10% each of zinc and chromium. Some confirmatory X-ray diffraction results are also included. With aluminium-rich alloys it has been possible to obtain conditions of true equilibrium by annealing treatments of the order of 2–3 weeks, but with some of the other alloys it has been found that when chromium is present, equilibrium cannot be obtained even after annealing treatments of many weeks.

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II.—Experimental Details.

1. *Materials Used.*

The aluminium used in the present work was super-purity metal kindly presented by the British Aluminium Company, Ltd. The zinc was from special zinc given by the National Smelting Corporation, to whom the authors must express their thanks. Spectrographic analysis showed that the metal contained the following impurities : lead 0·001, cadmium 0·001, copper 0·0016, iron 0·001, and zinc (by difference) 99·995%. The magnesium, of Canadian origin, was of 99·96% purity, and was supplied by the Light Metals Control Board. The chromium was introduced into the alloys in the form of master alloys, one of which was given by the National Physical Laboratory and the other by the British Aluminium Company, Ltd. The analyses of these two alloys are given below :

Source of Alloy.	Chromium, %.	Silicon, %.	Iron, %.	Copper, %.
N.P.L.	8·6	0·002	0·003	...
British Aluminium Company .	9·5	0·004	0·0025	0·001

2. *Preparation and Annealing of Alloys.*

The alloys were melted in crucibles lined with an alumina–fluorspar mixture, the general policy being to melt the aluminium and aluminium–chromium master alloy first, and then to add the zinc and magnesium. The whole was thoroughly stirred with an alumina stirrer, and was cast as soon as possible into a heavy copper mould to give an ingot of $\frac{3}{8}$ or $\frac{5}{16}$ in. dia. The alloys were sealed in evacuated hard glass tubes and were then annealed in tubular electric resistance furnaces controlled by Foster temperature regulators. The details of preparation and annealing technique have been described in previous papers.[1, 3, 5]

3. *Microscopic Examination of Alloys.*

The alloys were sectioned with a fine-toothed hacksaw and were then ground by hand and polished, the general methods being similar to those described in earlier papers.[1, 3, 5] The micro-constituents encountered in the ternary Al–Cr–Zn alloys were the α solid solution in aluminium and the two compounds $CrAl_7$ and Cr_2Al_{11}, of which the latter disappeared after long periods of annealing and was thus not an equilibrium constituent of the alloys concerned.

The compounds $CrAl_7$ and Cr_2Al_{11} are both hard and unreactive and appear as grey particles, often in considerable relief in the unetched

section. The particles of $CrAl_7$ are stained only by comparatively violent etching reagents. Of these the most suitable were found to be a hot 1% aqueous solution of caustic soda or a hot alkaline permanganate solution. The latter consisted of 1 part of 2*N*-sodium hydroxide and 10 parts of *N*/10-potassium permanganate, and was used at 60°–70° C. This solution deteriorates rapidly and must be prepared fresh for each alloy. When the two compounds are present in the same alloy, the general tendency is for the $CrAl_7$ to be attacked and stained more readily than the Cr_2Al_{11}, but the distinction is not always reproducible, and repeated etching and polishing is desirable before a conclusion is reached. Both the above-mentioned reagents are suitable for this purpose, and the alkaline permanganate solution is on the whole more reliable. Fig. 1 (Plate III) shows the microstructure of an alloy containing 7·65% chromium and 10·22% zinc after annealing for 26 days at 460° C. The micro-section shows one crystal of Cr_2Al_{11} surrounded by a sheath of $CrAl_7$, together with numerous crystals of the latter compound. This specimen was heavily etched with alkaline permanganate with the result that the α solid solution has been stained.

In the ternary system Al–Cr–Mg the phases encountered were the α solid solution, $CrAl_7$, a ternary phase denoted *E*, and chilled liquid. The ternary phase *E* is softer than $CrAl_7$, and in unetched sections it appears whiter in colour and in less relief than $CrAl_7$. *E* is not attacked by nitric or sulphuric acids, but is outlined by a 1-min. swab etch with 1% aqueous hydrofluoric acid. It may be distinguished from $CrAl_7$ by the alkaline permanganate reagent referred to above. With this reagent, $CrAl_7$ gives a brown tarnish and is more heavily attacked than the *E* phase, which shows at first a whitish blue-grey colour and turns brown only on prolonged etching. The chilled liquid in these alloys is revealed as a characteristic duplex structure by etching in concentrated nitric acid or by swabbing for 30 sec. in 1% aqueous hydrofluoric acid. Fig. 2 (Plate III) shows the microstructure of an alloy containing approximately zinc 2, magnesium 3, and chromium 6% after annealing for 33 days at 460° C. The section is polished but unetched and shows the α solid solution together with crystals of $CrAl_7$ surrounded by *E*.

III.—Description and Discussion of Results.

In order to appreciate the results it is necessary to consider first the equilibrium diagrams of the binary systems Al–Mg and Al–Cr, and these are reproduced in Figs. 3 and 4. In the system Al–Mg at 460° C. the phases met with in the range of composition with which the present paper is concerned are the α solid solution of magnesium in aluminium, and the liquid phase. The solidus point of the α solid solution at

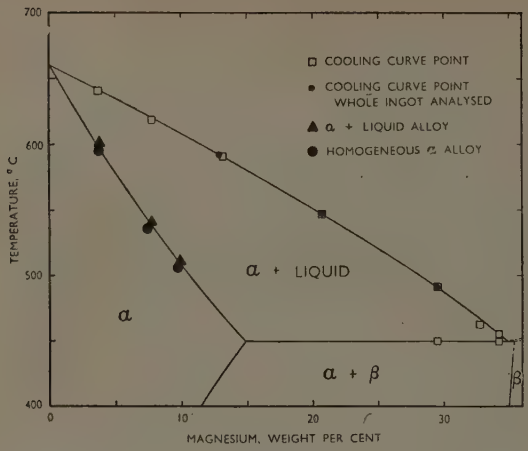

FIG. 3.—The Equilibrium Diagram of the System Aluminium–Magnesium.

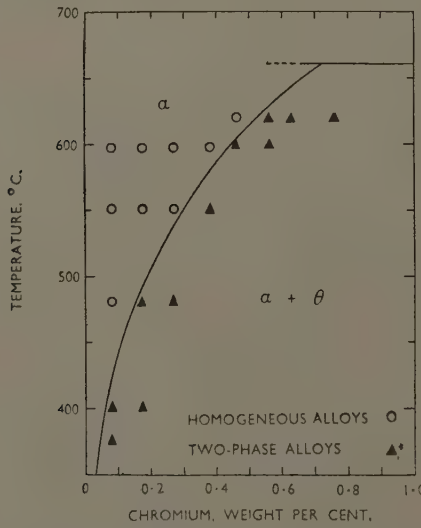

FIG. 4.—The Equilibrium Diagram of the System Aluminium–Chromium. (After Raynor and Little.)

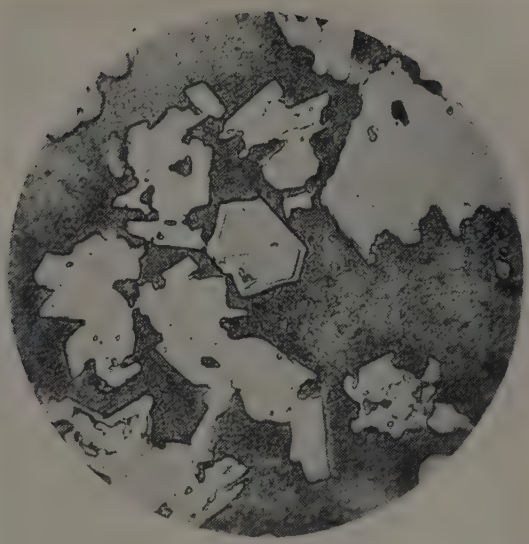

FIG. 1.—Microstructure of an Alloy Containing 7·65% Chromium and 10·22% Zinc After Annealing for 26 Days at 460° C. × 1000.

FIG. 2.—Microstructure of an Alloy Containing Approximately Zinc 2, Magnesium 3, and Chromium 6% After Annealing for 33 Days at 460° C. × 1000.

[*To face p.* 42

460° C. lies at approximately 14% magnesium.[8] In the system Al–Zn the alloys concerned are all within the α solid-solution range at 460° C. The system Al–Cr has been studied by Raynor and Little,[9] according to whom the solid solubility of chromium in aluminium decreases from 0·72% chromium at 660° C. to 0·13% chromium at 460° C.

1. *The System Aluminium–Chromium–Zinc.*

No previous detailed examination of this system appears to have been made, and the alloys whose compositions are represented by squares in Fig. 5 were therefore prepared and annealed for 26 days at 460° C. After this treatment the alloys represented by the symbols ▧ and ▨ were found to consist of the α solution together with $CrAl_7$ and traces of

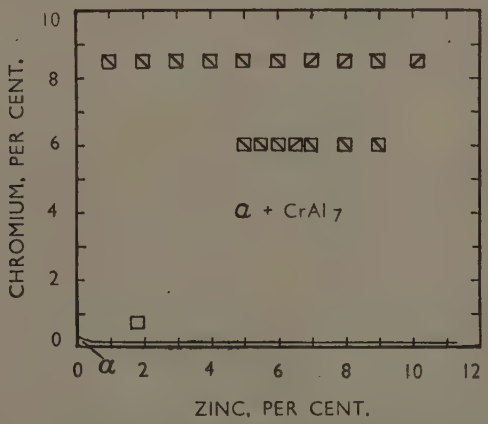

Fig. 5.—Alloys Examined in the System Aluminium–Chromium–Zinc.

Cr_2Al_{11}. It seemed very improbable that this could represent a true equilibrium condition, and the four alloys marked ▨ were therefore given a further annealing treatment of 31 days, making a total of 57 days at 460° C. After this further treatment, the Cr_2Al_{11} phase had disappeared, and the alloys were of the ($\alpha + CrAl_7$) type. It is thus clear that the traces of the Cr_2Al_{11} found in the alloys after the 26-day anneal were due to lack of equilibrium, and this was confirmed by the fact that inconsistent results were obtained when attempts were made to determine the tie lines by measurements of the lattice spacings of the α phase in the alloys annealed for periods of the order of 4 weeks. The results for the four alloys marked ▨ suggest that in the true equilibrium state the alloys shown in Fig. 5 will all be of the ($\alpha + CrAl_7$) type. Examination

showed that in the alloys containing 8·5 and 6% of chromium the Cr_2Al_{11} phase was present in the original castings, and that in many cases the particles of Cr_2Al_{11} were surrounded by a sheath of $CrAl_7$; it seems probable that this is one of the reasons for the sluggishness of the reaction $\alpha + Cr_2Al_{11} = CrAl_7$.

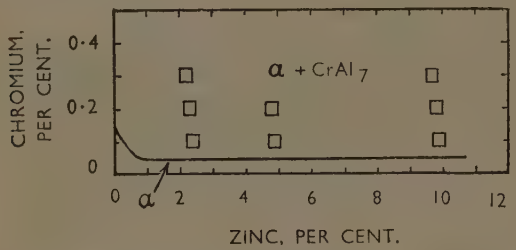

FIG. 6.—The System Aluminium–Chromium–Zinc. Equilibrium diagram of aluminium-rich alloys at 460° C.

In Fig. 5, the one alloy marked □, together with others of low chromium content, contained no particles of Cr_2Al_{11} in the original casting, and these alloys appeared to reach equilibrium very much more

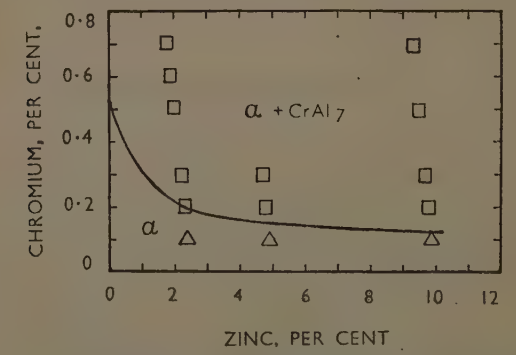

FIG. 7.—The System Aluminium–Chromium–Zinc. Equilibrium diagram of aluminium-rich alloys at 620° C.

rapidly. In Fig. 5 there is a very narrow area at the bottom of the diagram, representing the homogeneous α solid solution, but this is too restricted to be shown on the scale of the diagram. Fig. 6 shows the results obtained in this region of composition for the structures of alloys annealed at 460°C.

for 21 days, while Fig. 7 shows the solubility curve * at 620° C. as determined by annealing treatments of 12 days. It will be seen that at each temperature the solubility of chromium is diminished by the addition of zinc. These alloys were not analysed because other experiments had shown that with small percentages of chromium, the intended compositions were attained to a high degree of precision.

The microscopic work thus showed that under conditions of true equilibrium the stable phases in the alloys examined were α and $CrAl_7$, although in the alloys of higher chromium content Cr_2Al_{11} is present in the cast ingots and is removed only by very prolonged annealing. The

TABLE I.

Composition of Melt.		Percentages of Chromium and Zinc in Extracted Crystals of "$CrAl_7$".	
Cr, %.	Zn, %.	Cr, %.	Zn, %.
3·0	2·0	22·94	0·18
1·6	3·0	21·05	1·40
1·0	4·0	22·0	1·91
1·0	10·0	24·23	2·81

absence of any other phases was confirmed by the fact that Debye–Scherrer films of several poly-phase alloys contained only the lines characteristic of the α, $CrAl_7$, and Cr_2Al_{11} phases. In view of the difficulties of obtaining true equilibrium in these alloys, attempts to determine tie lines from lattice-spacing measurements were discarded, but as some work in this connection suggested a variation in the composition of the $CrAl_7$ phase, it was thought of interest to examine the composition of crystals of this compound extracted electrolytically from slowly cooled alloys, using the method of Raynor and Hume-Rothery.[2] The results of this work are given in Table I, from which it will be seen that the "$CrAl_7$" phase is able to take up zinc into solid solution, the percentage increasing with the zinc content of the melt.

2. *The System Aluminium–Chromium–Magnesium.*

The equilibrium diagram of this system has been investigated by Erdmann-Jesnitzer,[10] whose results are in substantial agreement with those of the present work as far as the general form of the diagram is concerned. The present results are shown in Fig. 8, which covers the range 0–20% magnesium and 0–10% chromium. Most of the alloys

* For the experiments at 620° C. the alloys were enclosed in alumina collars inside sealed glass tubes in order to prevent contact between the alloy and the glass.

shown in this diagram were annealed for periods of 16–25 days, but the critical alloys which were near to the boundary of a phase field were annealed for one month at 460° C. The alloys whose compositions are indicated by full squares or triangles are those which were analysed after the annealing treatment. The analytical results showed that the intended composition was attained satisfactorily provided that the chromium and magnesium contents were each less than about 5%. With

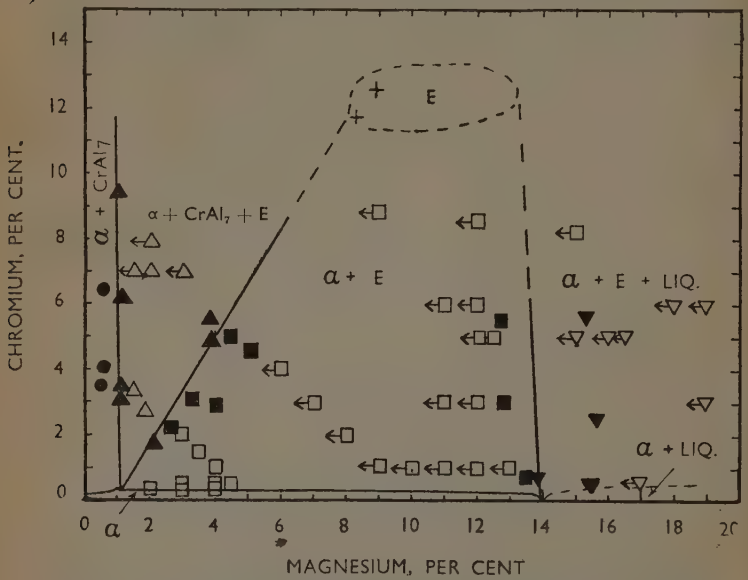

FIG. 8.—The System Aluminium–Chromium–Magnesium. Equilibrium diagram of aluminium-rich alloys at 460° C.

higher percentages of these elements there was a tendency for magnesium to be lost in melting, particularly when the chromium content was high. These alloys are therefore represented in the diagram by open squares and triangles with arrows pointing in the direction of lower magnesium content. It must be emphasized that such points do not indicate the actual composition of the alloys concerned, but the points are included in the diagram as evidence that the whole region of composition was explored thoroughly in order to ensure that no additional phases were present.

From Fig. 8 it will be seen that the solid phases met with in the range

of composition concerned are (1) the α solid solution, (2) the $CrAl_7$ phase of the binary system Al Cr, (3) a ternary phase denoted *E* which is of variable composition, and (4) the liquid phase. The phase fields lie in regular order as shown, and the results for aluminium-rich alloys are shown on a larger scale in Fig. 9, which includes points for some alloys whose compositions are too close together to be shown in Fig. 8. The apex of the 3-phase ($\alpha + CrAl_7 + E$) triangle meets the α solid-solubility curve at the point corresponding with 1·1% magnesium and 0·3% chromium. A measurement was made of the lattice spacing of the α

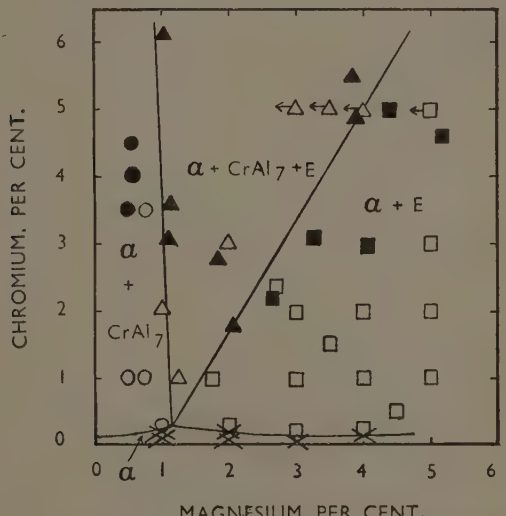

Fig. 9.—The System Aluminium–Chromium–Magnesium. Equilibrium diagram of aluminium-rich alloys at 460° C.

phase in an annealed 3-phase ($\alpha + CrAl_7 + E$) alloy, and this confirmed the composition of the α corner of the 3-phase triangle.*

As shown in Fig. 8, the *E* phase is of variable composition. The two points marked + represent the compositions of crystals of *E* extracted electrolytically by the method of Raynor and Hume-Rothery [2] from slowly cooled melts of ternary alloys. The details of the extraction are given in Table II, and it will be seen that the compositions of the two extracts lie almost exactly on the ($\alpha + CrAl_7 + E/\alpha + E$) side of the

* As shown by Axon and Hume-Rothery,[12] the lattice spacing/composition curve in the system aluminium–magnesium is not linear in the region 0–2% magnesium.

3-phase triangle as deduced by microscopic work. The direction of the ($\alpha + E/\alpha + E +$ liq.) phase-field boundary suggests that the E phase is

TABLE II.

Composition of Melt from which Crystals of E were Extracted Electrolytically.		Composition of Extracted Crystals.	
Cr, %.	Mg, %.	Cr, %.	Mg, %.
3·0	15·0	12·6	8·8
3·0	25·0	11·8	8·2

of variable composition, and this was confirmed by the fact that the lattice spacings of E were not constant. The crystal structure of E is

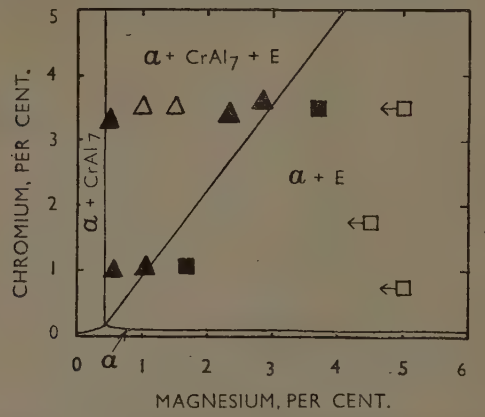

FIG. 10.—The System Aluminium–Chromium–Zinc–Magnesium. Equilibrium diagram of aluminium-rich alloys containing 8% zinc at 460° C.

cubic, with lattice spacing $a = 14{\cdot}65$ kX., and the unit cell probably contains 16 molecules of $Cr\,Mg_2Al_{12}$. Details of a goniometric and X-ray study of crystals of the E phase are being described elsewhere.[11]

3. *The Quaternary System Aluminium–Magnesium–Zinc–Chromium.*

In studying the quaternary system it was found convenient to prepare alloys with constant percentages of zinc, and to anneal them for one month at 460° C. In this way, if we regard the ternary system Al–Cr–Mg of Fig. 9 as lying in the basal plane of a quaternary model, we obtain the structures on horizontal sections across the model at constant percentages of zinc. Fig. 10 shows the structures of aluminium-rich alloys containing

8% zinc; the symbols in this diagram have the same meaning as those in Fig. 9. Within the range of composition covered by this diagram, no new phases are introduced, and the phase fields lie in the regular sequence ($\alpha + CrAl_7$), ($\alpha + CrAl_7 + E$), ($\alpha + E$), and α; the boundary between the ($\alpha + E$) and ($\alpha + E +$ liq.) fields was not investigated. The general form of the diagram in Fig. 10 is similar to that of Fig. 9, but the ($\alpha + CrAl_7$) field is slightly narrowed. In the ternary system Al–Mg–Zn, alloys containing 8% zinc can dissolve up to 4·8% magnesium before the α solid-solubility curve is exceeded, and with higher percentages of magnesium the alloys are of the ($\alpha + T$) type, where T denotes the ternary phase which is usually called $Al_2Mg_3Zn_3$, although it is actually of widely variable composition. It follows therefore that in Fig. 10 the ($\alpha/\alpha + T$) boundary will lie at 4·8% magnesium on the base of the Figure and that with higher contents of magnesium there will be an ($\alpha + T + E$) triangular field. In the present investigation the alloys examined did not contain sufficient magnesium for the T phase to have been encountered.

A series of 26 quaternary Al–Mg–Zn–Cr alloys containing 2% zinc was also prepared and annealed for 1 month at 460° C. Using the synthetic compositions, the observed microstructures were plotted in a diagram analogous to Fig. 10, and in this diagram the boundaries between the phase fields were identical with those of Fig. 9. In view of the very small displacement of the boundaries produced by 8% zinc, we may expect the effect of 2% zinc to be extremely small, and as this was confirmed by the diagram based on synthetic compositions, the alloys containing 2% zinc were not analysed. In general, therefore, the structures of the quaternary alloys containing up to 8% zinc are simple and can be readily understood, and interpolation may be used between Fig. 9 (0% zinc) and Fig. 10 (8% zinc).

As a matter of interest, crystals of the E phase were extracted electrolytically from a slowly cooled quaternary alloy containing chromium 3, magnesium 15, and zinc 1·5%. The analysis of these crystals indicated that they contained chromium 13·2, magnesium 12·2, and zinc 0·7%. Comparison of these figures with those obtained from the ternary Al–Cr–Mg alloys (see p. 50) shows that the magnesium content of the E phase can vary considerably, and that some zinc can be taken into solid solution.

ACKNOWLEDGEMENTS.

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THE MEASUREMENT OF GRAIN-SIZE OF TUNGSTEN AND TUNGSTEN CARBIDE POWDERS USED FOR THE MANUFACTURE OF HARD-METAL.* 1142

By H. BURDEN,† B.Sc., and A. BARKER,† B.Sc., A.R.C.S., A.Inst.P., L.I.M.

SYNOPSIS.

Several methods were employed for the examination of the particle size of tungsten and tungsten carbide powders used in the production of "hard-metal". A sedimentation balance and a turbidimeter both proved unsatisfactory, but a gross method using a Spekker absorptiometer gave good correlation with the particle size observed with an electron microscope.

The major difficulty in all the methods used was the effect of aggregation of particles.

The results show how tungsten of four different grain-sizes behaves during the processing to the finished hard-metal, the coarse powders tending to decrease in grain-size and the fine ones to increase.

A relationship has been established between the hardness of the finished metal and the particle size of the original tungsten.

I.—INTRODUCTION.

TUNGSTEN carbide–cobalt hard-metals need to have primarily a high hardness for the uses to which they are put. The hardness is governed by two main factors: the amount of cobalt present and the grain-size of the tungsten carbide phase in the finished metal. The grain-size of the tungsten carbide phase is influenced by the particle size of the original tungsten powder and grain growth during processing.

These factors have been discussed by E. W. Engle,[1] Rogers,[2] Meyer and Eilender,[3] and Sykes,[4] but precise experimental details of the methods used for measuring particle size have in no instance been given.

The main stages in the manufacture of tungsten carbide–cobalt hard-metal are:

1. Mixing the tungsten with carbon in a ball mill.
2. Carburizing the mixture of tungsten and carbon.
3. Ball milling the tungsten carbide.
4. Ball milling the tungsten carbide with cobalt.
5. Adding wax for lubrication during pressing.
6. Pressing the powder.

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† Brown–Firth Research Laboratories, Sheffield.

7. Pre-sintering.
8. Shaping.
9. Sintering.

All these stages, with the exception of 5, 6, 7, and 8, can affect the grain-size of the finished metal. Although ball milling rapidly breaks down aggregates, the crushing of single grains appears to take place much more slowly. Thus any significant reduction of grain-size involves protracted ball-milling times of say 60–100 days. For a number of reasons, ball-milling times are limited to 1–4 days in commercial production, so that the reduction in particle size by this means is negligible. Grain refinement cannot occur during carburizing and sintering. Generally, conditions during these stages are such that a net increase in particle size occurs over the whole process.

Thus, if a fine grain-size is required in the final product, the raw materials must have a small particle size and each stage of manufacture must be checked to limit the amount of grain growth that occurs. It is clear that an accurate and rapid assessment of particle size is of considerable value in controlling the quality of hard-metal on a production scale. From this point of view, the writers have investigated several methods of particle-size measurement. Using some of these methods, we have studied variations in particle size which occur during the production of a typical hard-metal and the effect of the initial particle size of the tungsten on the properties of the finished material.

II.—Methods Used for Particle-Size Determination.

The methods which have been used are as follows :

1. The sedimentation balance.
2. Richardson turbidimeter.
3. A gross method employing the Spekker absorptiometer.
4. Microscopic counts by optical microscope.
5. Examination by electron microscope.

1. *The Sedimentation Balance.*

The determination of particle-size distribution by the sedimentation balance has been described in detail by a number of workers.[5, 6, 7] The method consists of weighing the powder which sediments to a fixed level at various times after an initial dispersion in a suitable liquid. The apparatus best suited for this is a " Chainomatic " type of balance, one pan of which is suspended in a beaker containing the sedimenting liquid. From the rate of sedimentation the particle size may be calculated.

In our experiments the suspension was prepared by initially grinding the dry powder in an agate mortar with a rubber-covered rod to break up loose aggregates. The powder was then dispersed in a suitable liquid by stirring in the beaker, using the balance pan as stirrer, or, alternatively, the suspension was produced by shaking in separate equipment and then transferring to the beaker in the balance case. The concentration used in most experiments was 0·1 g./100 ml.

When the powder is fully dispersed the balance is counterpoised to give the zero reading. This must be done for each experiment as the buoyancy of the liquid may vary with different powders in suspension. Counterpoising must be done as quickly as possible, otherwise a faulty zero is obtained owing to heavier particles reaching the pan and being counted as part of the pan weight. Readings are then taken of increase in weight with time. These readings are plotted and usually give a smooth curve, from which the size distribution of the powder can be obtained by graphical means.

Stokes's law is used in calculating the size distribution from the weight increment–time graph. This only holds for spherical particles moving through a liquid under conditions of viscous flow. Thus the Reynolds number for the system must be low. Arnold [8] has shown that this must be less than 1·2 for viscous-flow conditions to occur. From this can be calculated the critical upper limit of particle size above which Stokes's law becomes increasingly inaccurate. This is 50 μ for tungsten in water. All the powders considered in this paper are believed to contain no particles greater than this.

The effect of Brownian movement is not taken into account in calculating the size distribution. However, no permanent colloidal suspensions occurred with any of the powders investigated. Taking into account the high density of the powders, the effect of Brownian motion will be small compared with the errors due to aggregation during sedimentation unless Brownian movement is a major factor in aggregation.

No correction for particle shape was made as none of the particles examined microscopically had any marked degree of asymmetry.

Further information on these sources of error is given in the literature.[9]

A difficulty of the method is the uncertainty of the initial weighing. This can, however, be repeated until a satisfactory start to the experiment is made. The effect of aggregation or breakdown of aggregates by prolonged handling should be reduced to a minimum. Reproducible readings can be obtained, but considerable practice is required and two separate observers do not check each other well. The method is not

sensitive enough to split up the — 1 μ fraction, owing mainly to the small weight concentration for a reasonable particle concentration and the effects of convection.

2. *The Richardson Turbidimeter.*

There are several types of turbidimeter described in the literature.[10, 11, 12, 13, 14, 15] An apparatus developed at the Imperial Chemical Industries, Ltd., from an original design by Dr. E. G. Richardson of King's College, Newcastle, has been used in this work. The apparatus is shown diagrammatically in Fig. 1 and may be described as follows.

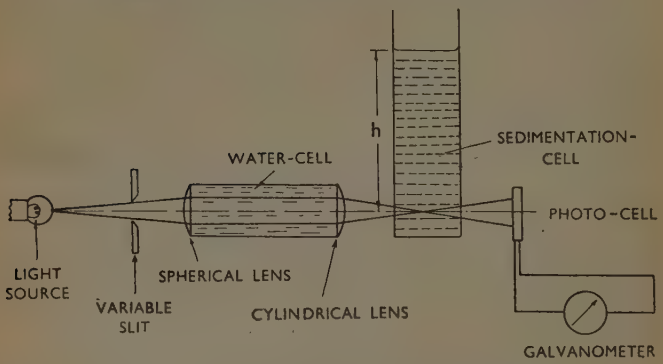


Fig. 1.—Optical System of Richardson Turbidimeter.

Light passes through a slit, is collimated by a spherical lens, passes through a water cell to reduce heat radiation, and then comes to a flat focus by way of a cylindrical lens. At this focal point is placed a glass sedimentation tank which contains the powder suspended in a liquid. The intensity of the light passing through the cell is measured by a photronic photo-cell and galvanometer. The entire optical system is placed on a platform which can be raised or lowered relative to the sedimentation cell, which is fixed.

The galvanometer readings are proportional to the intensity of the light I which passes through the suspension of powder in the cell. Hence the optical density, $\log_e \frac{I_0}{I}$, can be obtained, where I_0 is the intensity through the clear liquid.

As the powder gradually sediments out of suspension, the amount of light transmitted will gradually increase. From readings of the optical

density at known times, together with a knowledge of the depth h of the beam from the surface of the liquid (see Fig. 1), the size distribution of the powder in suspension can be calculated.

As very fine powders are slow in sedimenting, the optical system is moved up the cell in order to accelerate the determination.

The relationship between particle size and optical density used by us to calculate the size distribution is due to Heywood,[11] and is as follows:

$$\log_e \frac{I_0}{I} = \frac{1}{4} SCL \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where S is the specific surface of the powder (cm.^{2}/g.),
C is the concentration (g./ml.),
L is the length of the path of light through the liquid (cm.).

This is a modification of an earlier relationship by Werner.[16] The equation is based on particles totally blocking out an area of light equal to the projected area of the particles in a plane normal to the direction of the light beam.

Various workers have found that this equation does not hold good over the range 0·1–10 μ to which we have applied it, but wide differences of opinion occur. For further details in this connection, reference should be made to papers by Schweyer,[17] Schweyer and Work,[6] Richardson,[12,13] and Dalla Valle.[18]

Although the equation is not fundamentally correct, we believe that for the type of powders examined in this work it gives the correct order of size over the range 0·1–10 μ. This is demonstrated by comparing the results, given later, of the Spekker method and the electron-microscope photographs.

The remarks on Stokes's law made in the description of the sedimentation balance apply equally to this method.

Some difficulty was encountered in the use of the turbidimeter, owing to the light source giving a slowly varying intensity. This was largely overcome by using a battery of very large capacity, a uniform intensity being obtained after 15 min. working.

To reduce temperature fluctuations in the suspension, the sedimentation cell was carried in a large block of iron. The maximum temperature variation in the cell during an experiment was 2° C.

To test reproducibility obtainable with the turbidimeter, four tests were made on Type-II tungsten powder (details of the methods of preparation of the various types of tungsten used are given later). These were the first results obtained with the apparatus, so no skill in manipulation had been acquired by the operator. The results are

shown in Table I. The preparatory treatment of the suspension was 2 min. shaking in water.

TABLE I.—*Reproducibility of the Turbidimeter Method.*

Range,* μ.	Percentage by Weight in Range.			
∞–4	48·1	51·4	46·0	47·2
4–3	10·5	11·1	12·9	13·6
3–2	15·2	14·4	16·7	16·1
2–1½	10·8	9·9	11·2	9·3
1½–1	7·8	7·8	7·6	7·1
1–¾	6·1	4·5	5·0	4·8
¾–½	1·3	0·7	0·5	1·9
½–0	0·3	0·2	0·0	0·1

* $1\,\mu = 10^{-3}$ mm.

3. *The Use of the Spekker Absorptiometer.*

The Spekker absorptiometer may be used for determining the optical density of powder suspensions. The instrument gives direct readings of $\log_{10}\frac{I_0}{I}$. Using equation (1) the specific surface may be calculated if the concentration of the suspension and the cell length are known. As the Spekker absorptiometer is a well known laboratory instrument, no further description is given.

From the specific surface, the surface mean diameter can be obtained using the equation :

$$S = \frac{6}{d\rho} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where ρ is the density of the particles, d is the diameter of uniform spheres having the same specific surface as the powder measured.

Alternatively, equation (1) can be expressed in terms of d and ρ directly.

When the value of d expresses the mean size of a range of particle sizes, then, as calculated from equation (2), it is equivalent to the " surface mean diameter " d_s, defined as follows :

$$d_s = \frac{\Sigma nd^3}{\Sigma nd^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where n is the number of particles of diameter d.

A similar method for measuring specific surface has been described by Klein [19] and also by Sharratt, van Someren, and Rollason.[20]

Equation (1) has only a limited application with respect to concentration and cell length. Preliminary experiments showed that a concentration of 0·1 g./100 ml. and a cell length of 1 cm. were most suitable.

This method is very rapid. Using two operators, the total time taken for a set of results on one powder (i.e. four determinations) is under 10 min.

4. *Microscopic Count by Optical Microscope.*

Slides for microscopic examination were prepared by allowing drops of a suspension of the powder in water to dry on a glass slide. A large field was then photographed at a magnification of 100 dia. on a maximum-resolution plate. This photograph was subsequently enlarged to 1500 dia. and the actual count made from the enlargement.

5. *Microscopic Examination by the Electron Microscope.*

A Metropolitan-Vickers E.M.2 electron microscope was used at a magnification of 5000 dia. The specimen mount was the normal $\frac{1}{8}$-in.-dia. copper or nickel gauze, which was covered with a thin Formvar film. The specimens were prepared by spraying a suspension of the powder in water or ethyl alcohol on to the Formvar film or by allowing a drop of the suspension to dry on it.

III.—Investigation of Aggregation Phenomena.

The early work carried out, using some of the methods described above, showed that variations in the degree of dispersion of the powder in the suspending medium at the start of an experiment, and the effect of aggregation during the experiment, were primary causes of error. There are two factors to consider, firstly the initial aggregates present in the powder before being mixed with the suspending medium and secondly the rate at which aggregation occurs in the suspending medium. As we were concerned in measuring the true particle size of a powder and not the aggregate size, no differentiation has been made between these two factors in the work described below.

1. *Preliminary Tests.*

Equal weights of a given tungsten powder were shaken simultaneously with several different sedimenting media in test tubes. These were allowed to stand and the rate of sedimentation observed visually. The liquids fell into three distinct groups as follows :

Little Aggregation.	Medium Aggregation.	Severe Aggregation.
Water.	Nitro-benzene.	Ether.
Ethyl alcohol.	Benzaldehyde.	Petroleum spirit.
Aniline.	Ethyl benzoate.	Benzene.
	Ethyl acetate.	Paraffin.
	Amyl acetate.	Carbon tetrachloride.

The liquids in the right-hand column caused immediate aggregation of the powder; those in the left-hand column maintained a suspension for a considerable time.

2. *Experiments with the Sedimentation Balance.*

Size-distribution determinations were made on the same powder, using the sedimentation balance, with water, alcohol, and aniline as sedimenting media. The results are shown in Table II.

TABLE II.—*Effect of Different Sedimentation Media.*

Range, μ.	Percentage by Weight in Range.		
	Distilled Water.	Alcohol.	Aniline.
∞–12	6	0	0
12–10	3	0	0
10–8	3	1	1
8–6	6	7	30
6–5	4	10	26
5–4	9	17	23
4–2	53	50	21
2–0	16	15	0

These results show that water and alcohol are equally good, but that aniline causes some aggregation.

3. *Microscopic Examination.*

In order to have a reliable standard to which the results of aggregation experiments could be referred, an attempt was made to measure the size distribution of a standard powder by an optical microscopic count.

The powder when viewed at 1500 dia. contained two types of particles: smooth regularly shaped ones which could reasonably be assumed to be single grains, and those of irregular shape which appeared to be aggregates. These irregular particles were included in the count in two ways: assuming that they would behave as single particles in sedimentation, or assuming that they would break down into their constituent particles.

The results obtained by one observer for a count of 500 particles are given in Table III, together with the result of a sedimentation-balance test on the same powder.

It is clear that the aggregates observed microscopically are broken up under the conditions of the sedimentation test.

However, separate observers obtained differing estimates as to how an aggregate should be split up. It was therefore concluded that an

optical-microscopic count would not give a standard to which aggregation phenomena could be referred.

TABLE III.—*Comparison of Microscopic Count and Sedimentation Balance.*

Range, μ.	Percentage by Weight in Range.		
	Assuming Aggregates Broken Up.	Assuming Aggregates Remain as Aggregates.	Sedimentation Balance.
∞–8	12·6	7·6	6·3
8–6	...	18·1	4·7
6–5	...	14·4	5·6
5–4	7·2	19·0	12·3
4–2	62·5	46·0	53·0
2–0	17·9	4·9	18·1
Surface mean dia.	2·4 μ	3·3 μ	2·4 μ

It was then decided to use water as a sedimenting medium and to investigate the conditions under which a particular method gave the lowest size for a particular powder. At this stage the sedimentation balance was discarded in favour of the turbidimeter for the reasons given later.

4. *Experiments with the Turbidimeter.*

(a) *The Effect of Shaking the Suspension.*

The effect of shaking was observed on Type-IV tungsten powder. This powder was used because of its fine particle size, fine powders being suspected of aggregating to a greater extent than coarse ones. The powder was dispersed in distilled water in a 250-ml. flask. The half-filled flask was shaken by hand for various times up to 1 hr.

Table IV gives the results.

TABLE IV.—*The Effect of Shaking on Size Distribution.*

Range, μ.	Percentage by Weight in Range.			
	No Shaking.	15 min.	30 min.	60 min.
∞–4	29·8	20·9	14·1	18·2
4–3	8·0	2·0	5·1	2·7
3–2	10·3	6·7	8·8	5·3
2–1½	6·3	8·5	7·8	8·1
1½–1	11·5	19·8	14·7	17·4
1–¾	11·7	17·3	14·9	22·5
¾–½	13·2	24·2	31·4	23·5
½–0	9·2	0·5	3·3	2·4

It is concluded that there is a breakdown of large aggregates on shaking. Some particles below 0·5 μ in size appear to aggregate. After 30 min. shaking no further breakdown of aggregates occurs.

(b) *The Effect of pH on Size Distribution.*

Determinations were made on Type-IV tungsten, using various buffer solutions having *p*H values of from 1·17 to 12·38, as suspending liquids. Borate buffers were used on the alkaline side of water neutrality and citrate buffers on the acid side. The powders were shaken for 15 min. in the liquid before each test.

These liquids showed no general improvement on water as a dispersing medium, but acid solutions caused more aggregation than alkaline solution.

(c) *Wetting Agents.*

Some tests were carried out with wetting agents, in order to improve the dispersion of the powders in water. No conclusive results were obtained, certain wetting agents being effective with one tungsten powder but causing aggregation of others. It was considered best, therefore, not to use them.

5. *Preliminary Treatment of the Powder.*

The effect of preliminary grinding of the powder was investigated by measuring the apparent specific surface after various grinding times using the Spekker method. 2 g. of Type-III tungsten powder were ground in a small agate mortar by the rubber-covered end of a ¼-in.-dia. glass rod. The ground powder (1 g.) was shaken for 5 min. in 300 ml. of water in a 1000-ml. flask, then made up to 1000 ml. and gently agitated until thoroughly mixed.

The results are shown in Table V.

TABLE V.—*The Effect of Grinding Time on Specific Surface.*

Grinding Time, min.	Specific Surface, $cm.^2/g.$
0	780
0·5	2860
1·0	3040
1·5	4150
2·0	4250
2·5	4530
3·0	4880
3·5	5090
4·0	5030
4·5	5090
5·0	5230

The influence of this treatment on the breakdown of initial aggregates is very marked, a minimum time of 3 min. being required before the maximum effect is achieved.

6. *Conclusions.*

Water was chosen as the best dispersing agent of those investigated. Because of the errors in counting, it was found impossible to estimate accurately, by comparison with a microscopic count, the amount of aggregation occurring with any of the methods used.

Shaking the suspension breaks up some large aggregates, but tends to form small ones. Variations in *p*H cause no improvement on pure water. The preliminary grinding of the powder has a pronounced effect.

As the degree of aggregation was still unknown and as each step in the preparation of a suspension of powder appeared to affect it, the search for a perfectly dispersed suspension was abandoned, and the conditions were standardized so that reproducible and comparative results on different powders could be obtained. These conditions were :

(*a*) Grinding 2 g. of powder with a rubber-covered rod for 3 min.

(*b*) Vigorous shaking for 15 min. in a fixed quantity of water in a standard flask, the concentration of the suspension then being adjusted to a suitable value by the addition of more distilled water, followed by a few gentle shakes.

(*c*) The concentration used for the turbidimeter varied from 0·01 to 0·08 g./100 ml., depending on the particle size of the powder, it being found that the determination could best be made if the initial optical density was approximately the same for each powder. A concentration of 0·1 g./100 ml. was found to be most suitable for the Spekker method.

IV.—Types of Powder Examined.

Four types of tungsten were employed. The methods by which they were produced are given in Table VI.

Table VI.

Type.	Raw Material.	Reducing Agent.	Temp. of Reduction, °C.	Type of Furnace Treatment.
I	Tungstic oxide	Carbon	1250	...
II	,, ,,	Hydrogen	950	Batch
III	Ammonium paratungstate	,,	900	Continuous
IV	Tungstic acid	,,	900	,,

Indirect evidence suggested that the particle size of powders varied over a wide range. The particle size of the four powders was investigated at various stages during processing to the finished "alloy" powder. The stages of processing were:

(1) Ball milling the tungsten powder with 6·12% carbon for 24 hr.

(2) Carburizing the tungsten + carbon mix in graphite crucibles in a hydrogen atmosphere at 1420° C. for 3 hr.

(3) Breaking up the friable mass of tungsten carbide by ball milling for a further 24 hr.

(4) Adding 6·25% cobalt powder and ball milling with water for 72 hr.

(5) Sieving the dried cake through a 100-mesh sieve.

Samples were taken, for particle-size analysis, of the original tungsten powders and after operations (3) and (5).

TABLE VII.—*Turbidimeter Results on the Four Types of Powder.*

Stage of Process.	Range, μ.	Percentage by Weight in Range.			
		Type I.	Type II.	Type III.	Type IV.
Tungsten metal	∞–18	32·2	16·2	21·1	19·9
	18–14	22·9			
	14–10	17·1			
	10–8	6·9			
	8–6	5·2	16·1		
	6–4	5·3	21·7		
	4–3	3·2	10·8	9·2	6·9
	3–2	3·5	12·9	13·4	11·1
	2–1½	1·9	9·8	12·9	8·3
	1½–1	1·1	7·3	13·1	9·1
	1–¾	0·4	4·5	14·5	13·4
	¾–½	0·2	0·7	9·3	14·7
	½–0	0·1	0·0	6·5	16·6
WC after 24 hr. dry milling	∞–4	49·0	55·7	10·2	7·0
	4–3	12·8	10·9	6·4	0·0
	3–2	16·2	11·3	14·2	0·6
	2–1½	9·8	8·7	17·3	5·1
	1½–1	7·2	7·7	21·2	16·2
	1–¾	3·9	5·2	19·8	22·0
	¾–½	0·9	0·5	8·9	25·4
	½–0	0·2	0·1	2·0	23·7
Prepared alloy powder, dried and sieved through 100-mesh screen	∞–4	37·4	38·9	37·7	27·1
	4–3	14·1	13·3	8·8	6·6
	3–2	16·1	15·4	11·5	8·0
	2–1½	10·5	11·3	12·2	8·7
	1½–1	8·2	12·1	18·7	15·7
	1–¾	7·3	6·9	15·4	18·9
	¾–½	5·0	1·7	5·0	13·3
	½–0	1·4	0·4	0·7	1·6

V.—Experimental Results.

Tables VII and VIII give the results obtained with the turbidimeter and Spekker absorptiometer respectively on the four types of tungsten, the carbide, and the " alloy " powders prepared from them.

The turbidimeter results given are the mean of two separate determinations for each powder. The Spekker results are obtained from the mean of eight determinations of optical density from two suspensions of the given powder. The standard deviation of the individual results on each powder is given, from which it can be seen that the reproducibility of the method is good. The greatest variation occurs with the finest powders. This is believed to be due to the relative ease with which fine powders aggregate in water as compared with coarser ones. This point is discussed in Section VI.

Table VIII.*—*Results Obtained with Spekker Absorptiometer.*

Type of Tungsten Powder.	Stage of Process.								
	Tungsten Metal Powder.			Tungsten Carbide After 24 hr. Dry Milling.			Prepared Alloy Powder, Dried and Sieved Through 100-Mesh Screen.		
	Specific Surface, $cm.^2/g.$	Standard Deviation, $cm.^2/g.$	Surface Mean Dia., μ.	Specific Surface, $cm.^2/g.$	Standard Deviation, $cm.^2/g.$	Surface Mean Dia., μ.	Specific Surface, $cm.^2/g.$	Standard Deviation, $cm.^2/g.$	Surface Mean Dia., μ.
I	322	11·4	9·65	2560	23·5	1·49	4050	115	0·99
II	1760	44·2	1·77	1800	30·6	2·12	5080	46·0	0·79
III	4720	33·2	0·66	5920	29·6	0·64	5450	39·1	0·73
IV	14500	382	0·21	8390	193	0·46	6400	77·6	0·62

* The standard deviation in each case was calculated from eight specific-surface readings.

The same powders were examined by means of the electron microscope, and typical photographs are reproduced in Figs. 2–9 (Plates IV and V). Types-I, -III, and -IV tungsten powders, and the tungsten carbide and finished " alloy " powder from Types-I and -IV tungsten, are shown. The main purpose was to examine particle shape, and no attempt was made at a statistical particle-size count, owing to the difficulty of preparing specimens. However, the photographs shown were selected to be as representative of the particular powders as the examination of many fields in several specimens would allow. Therefore, a qualitative comparison of size can be made with the Spekker and turbidimeter results.

VI.—Discussion of Results.

1. *The Methods Used.*

Aggregation was the main difficulty in arriving at a sound method for particle-size measurement. All the methods described are affected in some way by aggregation. At this stage of our knowledge of aggregation phenomena, all that has been done is to standardize conditions to obtain reproducible results, as indicated previously.

Table IX compares the surface mean diameter of the four types of tungsten as calculated from the turbidimeter distribution curve, with the results obtained by the gross method, using the Spekker absorptiometer.

Table IX.—*Comparison of Spekker and Turbidimeter Results.*

Type of Tungsten.	Surface Mean Diameter, μ.		
	Determined by the Spekker Absorptiometer.	Calculated from the Turbidimeter Distribution Curves.	
I	9·65	8·11	0·84
II	1·77	2·87	1·62
III	0·66	1·15	1·74
IV	0·21	0·78	3·64

The factor ξ is the ratio of the turbidimeter mean size to that obtained with the Spekker. This factor is greater for fine powders than for coarse ones, which is to be expected if a fine powder aggregates more readily than a coarse one during suspension. Heywood [14] has used the ratio of the specific surface calculated from the initial turbulent reading, given by a turbidimeter type of apparatus, to that calculated from the distribution curve, to indicate whether aggregation has occurred during a particular experiment. He states that if no aggregation occurs, this factor has a value of 1·4–1·6, depending on the shape of the particles. The factor ξ is similar to Heywood's factor, except that the two readings involved come from different experiments, in which the optical arrangements are not exactly alike. On Heywood's basis, Types II and III are suitable for measurement by the turbidimeter without further precautions to prevent aggregation during an experiment. Type IV is too fine, a large amount of aggregation occurring, and Type I is too coarse, possibly giving erroneous results owing to very rapid settling in water. It is suggested that the large amount of aggregation occurring during sedimentation of Type-IV tungsten is due to translational Brownian movement increasing the

number of contacts between particles, this particular powder approaching the size at which the Brownian-movement effects are shown. Table IX shows that aggregation during sedimentation can occur to a considerable extent with some powders. Thus, rapid methods of the Spekker type are less prone to such errors.

The sedimentation balance was abandoned at an early stage of the work. The time needed to carry out a determination (4–6 hr.) was excessive for the purpose of works control, and the reproducibility was mainly governed by the operator's skill. The minimum size that could conveniently be dealt with was 1 μ, owing to the protracted time of fall of smaller particles, a 0·4-μ particle of tungsten falling through a distance of 10 cm. in 20 hr.

The turbidimeter was found to be an improvement on the sedimentation balance. The time of determination was usually 3 hr., of which only $\frac{1}{2}$ hr. was taken up by experimental work, but this was still lengthy for the purpose of works control. Reproducibility was good provided that sufficient care was taken to standardize the aggregation conditions. No special skill was required by the operator. A smaller concentration of powder in the sedimenting liquid was needed compared with that used in the sedimentation-balance method. This would reduce errors due to hindered settling and aggregation.

The Spekker method, like the turbidimeter method, suffers from an insecure foundation, the same basic light-absorption equation being used. It has an additional shortcoming in that the size distribution is not evaluated, but only the specific surface. However, the advantages of this method far outweigh the disadvantages. It requires no special skill to operate. A complete determination can be carried out in 10 min., which makes possible its use as a means of production control. By comparing the photographs of the powders shown in Figs. 2–8 (Plates IV and V) with the surface mean-diameter results of Table VIII, it can be seen that the Spekker results are in good agreement with the true size of the powders over the whole range of sizes examined. This is surprising in view of the theoretical limitations of the light-absorption equation, especially in the case of Type-IV tungsten, for which we estimate the true mean size to be between 0·1 and 0·15 μ, from the electron-microscope examination. It is difficult to decide at this stage whether this good correlation between Spekker readings and particle size is a simple effect as exemplified by the absorption equation, or is due to the combination of uncontrolled factors, such as aggregation, and some optical effect. The results reproduce well, as shown by standard-deviation figures.

The microscopic methods were most useful for particle-shape studies. An accurate determination of size distribution by direct

microscopic count was found to be impossible with the types of powder examined owing to the difficulty of making slides on which the powder was not aggregated. The assessing of an aggregate into its constituent particles was found to be unreliable. Even with suitable specimens the method would be unduly lengthy, and so it was not considered for control purposes. The resolution of an optical microscope is insufficient to deal with powders similar to Type-IV tungsten, and use was made of electron microscopy. Specimen preparation was even more difficult in this case, and in view of the possible divergence from random sampling that conditions in the microscope and specimen preparation might cause, no counts are given in this paper.

It is concluded therefore that of the methods discussed above, none is suitable for accurate size-distribution measurements on the types of powder to which we have applied them. For a rapid method, the most promising direction for further work seems to be the development of an improved turbidimeter, coupled with a greater knowledge of aggregation, sedimentation phenomena, and light absorption by particles.

For the time being, the Spekker method is used as our basic means of measuring particle size, supplemented where necessary by microscopic examination for shape and to indicate size range.

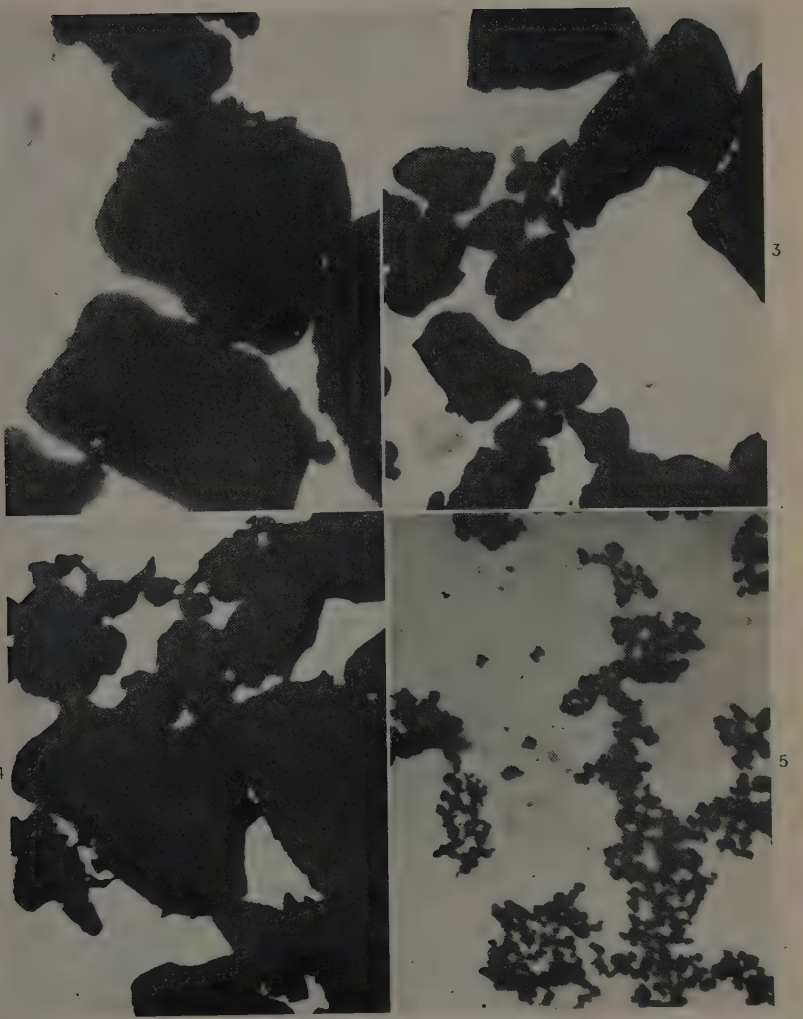
2. *Application of the Methods.*

The Spekker and the turbidimeter results indicate comparable effects on processing the four types of tungsten. Type-I material becomes much finer on ball milling after carburization. This is no doubt due to the breakdown of tightly bound aggregates that are believed to form when the oxide is reduced to metal. The breakdown of these aggregates is not complete at this stage, as is shown by the further reduction in size during the milling period in which the cobalt is mixed with the carbide.

Type-IV tungsten increases in particle size during carburizing owing to grain growth, while ball milling does not cause any reduction. Further coarsening then occurs, owing to the cementing together of particles by the soft cobalt during the ball milling of the carbide with this metal.

Types II and III are intermediate between Types I and IV in their behaviour.

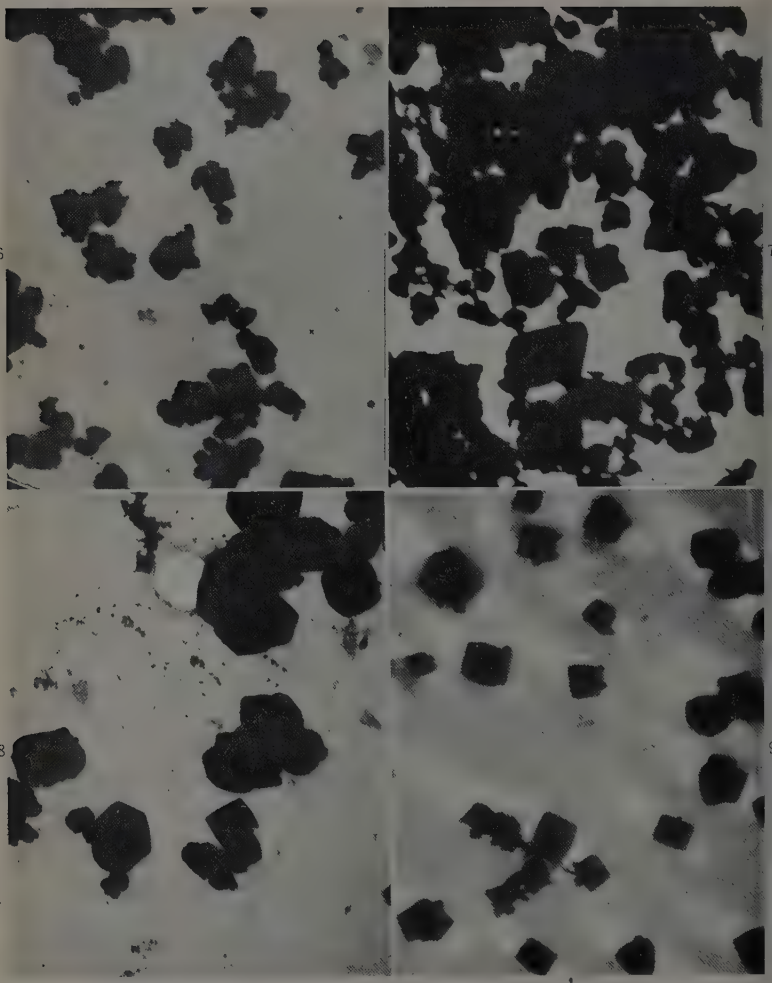
The above-quoted effects are also shown in the electron-microscope photographs (Figs. 2–9, Plates IV and V). Fig. 9 shows the cobalt powder used in this work. The characteristic grain shape of cobalt is absent in the "alloy" powder photographs. This may be due to the cobalt smearing itself on the tungsten carbide grains, a view previously



FIGS. 2–5.—Electron Micrographs of Powders and Finished "Alloy" Powders.

FIG. 2.—Type-I tungsten powder.
FIG. 3.—WC made from Type-I tungsten powder.
FIG. 4.—Alloy powder (WC + 6·25% Co) made from Type-I tungsten powder.
FIG. 5.—Type-IV tungsten powder.

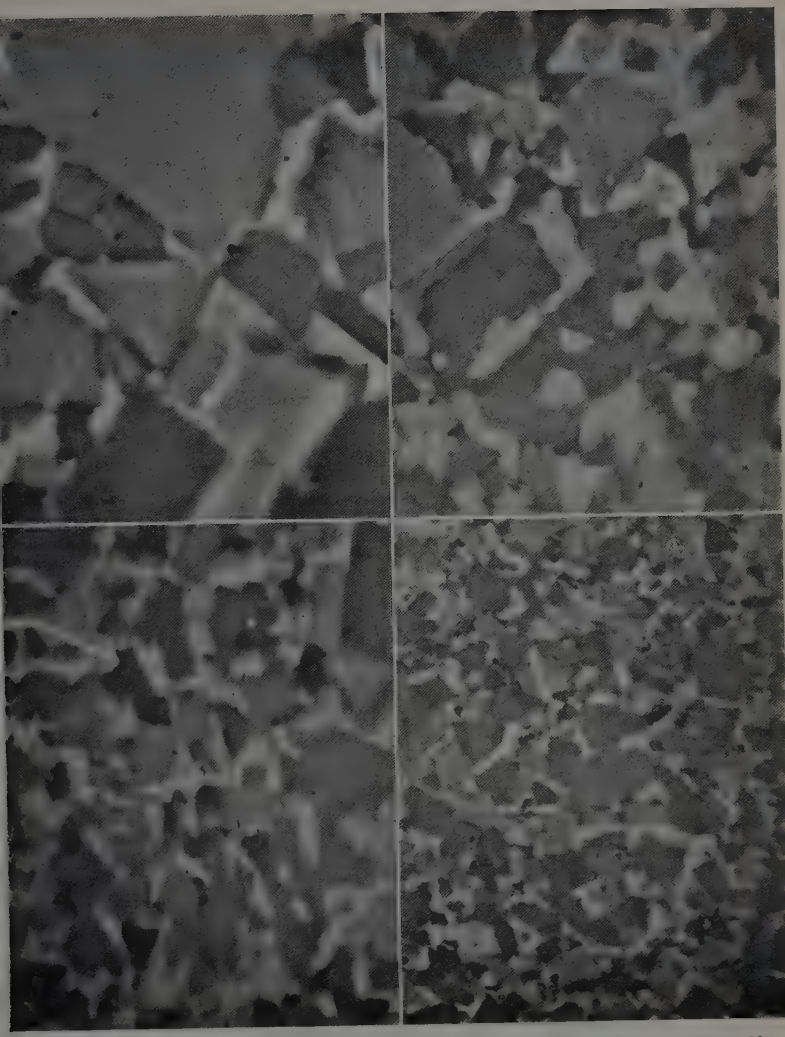
[*To face p.* 66.



× 10,000.

FIGS. 6–9.—Electron Micrographs of Powders and Finished " Alloy " Powders.

FIG. 6.—WC made from Type-IV tungsten powder.
FIG. 7.—Alloy powder (WC + 6·25% Co) made from Type-IV tungsten powder.
FIG. 8.—Type-III tungsten powder.
FIG. 9.—Cobalt metal powder.



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× 10,000.

FIGS. 10–13.—Electron Micrographs of Powders and Finished " Alloy " Powders.

FIG. 10.—Sintered alloy from Type-I powder.
FIG. 11.—Sintered alloy from Type-II powder.
FIG. 12.—Sintered alloy from Type-III powder.
FIG. 13.—Sintered alloy from Type-IV powder.

expressed by Hoyt.[21] Further evidence for this theory is given by the "spikes" on the outline of the tungsten carbide particles, which appear for the first time on adding cobalt.

Sintered pieces were prepared from the four types of powder. The sintering conditions were chosen to give the highest hardness, these conditions being determined separately for each type of powder. Table X shows the hardness of the finished hard-metal.

TABLE X.—*Hardness of Finished Alloys Prepared from the Four Types of Tungsten.*

Hard-Metal Prepared from Tungsten Powder of Type—	Hardness.	
	Rockwell A.	Diamond Pyramid No.
I	88·3	1220
II	90·8	1540
III	91·2	1590
IV	91·7	1650

The hardness thus depends on the particle size of the initial tungsten from which the four specimens were made and also on the particle size of the "alloy" powder. The variation in surface mean diameter measured by the Spekker method for a given change in hardness, is great enough to overshadow any error in the size measurement and makes this method convenient for control of hardness in production and for allocating batches of powder.

Figs. 10–13 (Plate VI) are electron micrographs of the sintered alloys, using a Formvar film replica technique. This method was used because of the difficulty of resolving the Type-IV alloy by optical means. All the specimens were etched in Murakami's reagent for 10 sec. before replicas were taken. It can be seen that little grain growth has occurred during sintering, and that the grain-size of the sintered specimen is in line with the particle-size determinations on the "alloy" powder.

While the investigation was in progress, large quantities of the four types of tungsten powder were used for production work, and their behaviour was consistent with the findings given above. For these particular types of powder and the methods used to process them, a quantitative relationship between hardness and surface mean diameter has been evolved.

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PRIMING PAINTS FOR LIGHT ALLOYS.* 1143

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SYNOPSIS.

The protection afforded to aluminium and magnesium alloys by various paint primers is being investigated in rural, industrial, and marine atmospheres.

The results have so far shown that, of the primers commonly used on other metals, iron oxide primers provide useful protection, whereas red lead primers are definitely harmful on aluminium, and especially so on magnesium. Primers pigmented with zinc chromate and zinc tetroxychromate are providing most efficient protection to light alloys.

I.—INTRODUCTION.

THE tests to be described in this paper were designed to determine the relative effectiveness of certain pigments in preventing the corrosion of aluminium, and aluminium and magnesium alloys, when used in priming paints under a range of atmospheric conditions. Commercial primers are normally based on complex mixtures of pigments containing varying proportions of corrosion inhibitors, non-reactive colouring materials, and extenders, the latter being necessary in order to improve the physical properties of the paints, such as freedom from settling, &c. It was thought advisable for this investigation, however, to use single pigments only, to simplify comparison and reduce the total number of specimens required.

The four pigments selected were zinc chromate, zinc tetroxychromate, iron oxide, and red lead. Zinc chromate was a natural choice since this corrosion-inhibiting material is used extensively for painting light alloys and has also proved very effective on iron and steel. Although zinc tetroxychromate has not been employed extensively so far in this country, it has been used with success in the United States, where it is frequently mentioned in specifications as an alternative to zinc chromate. One of the authors (J. G. Rigg) had previously found from long-term exposure tests that this material, despite a much

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lower chromium trioxide content, compared very favourably with zinc chromate on light metals and mild steel. Both iron oxide and red lead were included as examples of pigments commonly used in the building and engineering industries for priming ferrous metals. Iron oxide is of further interest since it is frequently employed in conjunction with zinc chromate and extenders in commercial light-metal priming paints and since it is a purely physical pigment; whereas the other pigments tested, such as red lead and zinc chromates, can provide chemical inhibition of corrosion of the underlying metal. While red lead is generally acceptable as a primer for both ferrous metals and wood, it is important to determine definitely whether it can be used safely on light alloys, since there is a wide belief that lead compounds are harmful to light alloys. It has been shown that lead pigments in the form of water pastes stimulate severe corrosion with magnesium alloys,[1] but the present authors are not aware of any previously published evidence of the unsuitability of red lead priming paints.

In addition to the light alloys, mild-steel specimens have also been tested, since all the pigments in the series are known to give effective primers for this metal and a useful comparison is thus provided; the mild steel also provides a basis of comparison with experience in the building and engineering industries. In order to obtain early indications of the relative performances of the pigments, some of the test specimens have been exposed with single coats of primers only and without top coats. Final conclusions, however, must be based on complete paint systems. Two types of commercial aluminium-pigmented finishes were chosen for the top coats, as being representative of high-quality paints with good water resistance, and these were based respectively on cellulose and medium oil length alkyd resin varnishes.

II.—Details of Materials.

Four priming paints containing, respectively, zinc chromate (specification D.T.D. 377A), zinc tetroxychromate, red lead, and iron oxide as the only pigments were made up in a ball mill using an oil varnish medium (Cerrux K4461) which is compatible with top coats to either specification D.T.D. 63A or D.T.D. 260A. Top coats were formulated with cellulose medium (D.T.D. 63A) and with a medium oil length linseed modified alkyd resin (D.T.D. 260A), using aluminium paste in both vehicles. All the paints were as reasonably near commercial-standard products as the use of single-pigment primers permitted. Cobalt naphthenate driers were employed for all the primers and the

D.T.D. 260A top coat. Further details of the paint formulations are given in the Appendix.

The results of physical tests on the priming paints are shown in Table I. The chemical analyses of the metals tested are given in Table II; mild-steel specimens were included for comparison. The wrought specimens measured 4 × 3 in. for the accelerated tests and 9 × 8½ in. for the field tests, while the cast bars were machined to 0·8 in. dia. × 7 in. long.

Specimens were exposed in triplicate in the following conditions:

1. Untreated (control specimens).
2. With pre-treatment as for painting, i.e. chromate treatment for magnesium-base alloys and pickling for other metals.
3. As 2, but painted with one coat of primer only.
4. As 2, but with two coats of primer and one of top coat.

Aluminium, B.S.S. 5L3, and steel specimens were degreased in trichlorethylene vapour in accordance with specification D.T.D. 915A; control specimens were exposed in this condition. The remaining aluminium and 5L3 specimens were etched in chromic–sulphuric acid solution in accordance with D.T.D. 915A, while the remaining steel specimens were pickled in 10% sulphuric acid solution, washed, and dried.

Pre-treatment of the magnesium-base alloys was as follows: D.T.D. 118 and D.T.D. 120A specimens were scoured with wet pumice powder, pickled in hydrofluoric–nitric acid, and then treated according to specification D.T.D. 911 (D.T.D. 118 specimens in the acid chromate bath (iv) and D.T.D. 120A specimens in the 30-min. R.A.E. bath (iii)); the cast specimens to specification D.T.D. 59A were cleaned in 5% boiling caustic soda after machining and treated according to specification D.T.D. 911 (in the 30-min. R.A.E. bath (iii)).

The primers were applied by brush, and the top coats by spray. Where no top coats were applied, single priming coats were used; in other cases two priming coats, followed by a misting top coat and then a full top coat, were applied. All the specimens were painted by one operator and were allowed to age for a period of one month after coating the last specimen. Painted specimens were then scratched with steel needles (to simulate mechanical damage). The scratches were made diagonally on the sheet specimens and longitudinally on the cast specimens, and penetrated the paint films to expose the bare metal.

III.—Exposure Conditions.

Specimens are exposed in field tests at Frodsham, Cheshire (rural); Widnes, Lancashire (industrial); Dungeness, Kent (marine); and in

TABLE I.—*Physical Tests on Priming Paints.*

	Zinc Chromate.	Zinc Tetroxy-chromate.	Iron Oxide.	Red Lead.	Specification Required by D.T.D. 63A.
Surface:					
Dry (min.)	45	45	45	45	Not specified.
Hard dry (hr.) . . .	5–6	5–6	5–6	5–6	Primer not more than 8 hr. Top coat not more than 2 hr.
Bend test at 0° *C.*					
Satisfactory over mandrel of given minimum size (in.) .	3/8	3/4	5/16	5/16	1/4
Scratch test.					
Max. weight (g.) which does not give scratch . . .	1300	1200	700	500	1000
Resistance to lubricating oils .	Slight film removed.	Slight film removed.	Complete film removed.	Satisfactory.	Satisfactory.
Resistance to organic solvents .	Blistering.	Blistering.	Film removed on rubbing.	Film removed on slight rubbing.	Satisfactory.

TABLE II.—*Analyses of Metals Included in Tests.*

Mark.	Material.	C, %.	Si, %.	Fe, %.	Cu, %.	Mn, %.	Zn, %.	Mg, %.	Al, %.	S, %.	P, %.
A	Pure aluminium	...	0·24	0·31	0·008	0·008	0·010	...	*	...	...
D	B.S.S. 5L3	...	0·54	0·40	3·95	0·59	0·018	0·60	*	...	...
Z	D.T.D. 120A high-purity base	...	0·006	0·0005	0·006	0·42	0·93	*	6·10	...	...
Y	D.T.D. 118 normal-purity base	...	0·005	0·021	0·004	1·54	0·005	*	...	...	...
V	D.T.D. 59A normal-purity base	...	0·010	0·022	0·002	0·28	0·59	*	7·70	...	...
W	D.T.D. 59A high-purity base	...	0·010	0·0010	0·002	0·18	0·58	*	7·83	...	...
S	Steel	0·16	<0·01	*	...	0·26	...	...	...	0·040	0·027

* Remainder.

an accelerated test at Gerrards Cross, Buckinghamshire, where they are sprayed with sea water twice daily when weather conditions permit. The test specimens are arranged so that both sides are exposed to the atmosphere, but only one surface is exposed to the sun. By mounting specimens at angles to the horizontal corresponding to the angles of latitude of the testing sites and facing due south, maximum exposure of the top surfaces to sunlight is obtained all the year round.

Care has been taken to avoid harmful bimetallic contacts, especially with the magnesium specimens. The wrought magnesium specimens in the accelerated test are suspended at all four corners by nylon thread. Magnesium sheet specimens at Dungeness are secured by galvanized iron nails with laminated plastic collars. Aluminium, 5L3, and steel specimens in the accelerated test and at Dungeness are secured by galvanized iron nails. Wrought specimens at Frodsham and Widnes are slipped over wooden pegs. Cast bars at all the stations are held in notched racks of laminated plastic sheet. So far, these methods of erection have proved satisfactory.

IV.—Methods of Examination of Specimens.

Specimens have been inspected after approximately one, two, four, and six months' exposure. A complete singleton withdrawal of the light-alloy specimens carrying single coats of primer has been made at all except the rural station, where failure has been so slight that only red lead primed panels have been removed. Some of the specimens involving the worst combinations of paint, metal, and environment have been withdrawn completely. The specimens remaining on test have been exposed for about one year at all sites. No steel specimens have been withdrawn yet, since they are not exposed in replicate at any station and they are required as controls.

Inspections were made at the sites without handling the specimens, but withdrawn specimens were examined in detail with the aid of a binocular microscope, before and after cleaning. Paint was removed by organic solvents. Corrosion products were removed from aluminium-base alloys by pickling at room temperature in concentrated nitric acid containing 5% chromic acid until the specimens were clean enough to permit detailed examination. Corrosion products were removed from magnesium-base specimens by treatment in 10% ammonium chromate in distilled water with air bubbled through the solution at frequent intervals.

The corrosion of the metal was assessed for type, number, size, and depth of areas of attack by the method described elsewhere,[2]

except that only one depth chart (*D*) was used for assessing the depth of both general and localized corrosion; corrosion occurring within ½ in. of the edge or the fixing holes of specimens, or in the vicinity of the scratch line, was recorded separately. Owing to the large number of specimens involved, the detailed results of examinations are not given in this paper. The standard terms derived from the three charts used in assessment are represented by one standard term only, the main weight being given to the chart for assessing the depth of attack. The deterioration of the paint film was assessed by a modification of the method used for corrosion, and the following factors were recorded separately: gloss, colour, chalking, checking, cracking, and flaking.

V.—Results.

The results of physical tests on the paints are recorded in Table I. The results so far obtained from corrosion tests are summarized below and in Tables III and IV. Fig. 1 (Plate VII) indicates the condition of some of the test specimens. Specimens with zinc chromate and zinc tetroxychromate primers do not show more than slight corrosion of any of the metals, even without top coats and in the most severe exposure conditions. It is therefore too early to assess the relative merits of these two chromates, and no further reference is made to them in the following results. The severity of the exposure conditions decreases in the order: Dungeness (marine), sea-water spray (accelerated test), Widnes (industrial), and Frodsham (rural).

1. *Marine Station and Accelerated Tests.*

Apart from much greater exposure to wind at the marine station, which encourages flaking of the top coats, more especially from the scratch lines, the specimens at these two exposure stations behaved in a similar manner, and the relative merits and disadvantages of the various materials are the same for the two sites.

Table III gives a summary of the detailed results obtained in the accelerated tests after thirty weeks' exposure.

All the aluminium and magnesium alloy specimens treated with red lead primer have suffered considerably more corrosion than the corresponding unpainted specimens. Indeed, some of the red lead painted metals without top coats were severely corroded after six weeks' exposure, while severe corrosion had also occurred even with top coats. Thus red lead has accelerated the corrosion of light alloys and, more especially, of the magnesium-base alloys. No acceleration of corrosion has been observed with the other primers tested.

Painting.			Magnesium Alloys.		Aluminium (Alloys).	
Mark.	Primer.	Top Coat.	High-Purity D.T.D. 120A (*Z*).	Normal-Purity D.T.D. 118 (*Y*).	Alloy B.S.S. 5L3 (*D*).	Pure Aluminium (*A*).
b	None	None				
c	Chromate	None				
e	Red lead	None				
f	Iron oxide	None				
n	Red lead	D.T.D. 260A				

FIG. 1.—Cleaned Specimens After 30 Weeks' Exposure in the Accelerated Test.

[*To face p.* 74.

Both red lead and iron oxide provided considerable protection to steel for some weeks, even when applied as a single coat without a top coat. The chromate primers, however, appear in general to be more protective on the metals tested, though the superiority over iron oxide primers is not very pronounced at the present stage of these tests.

Fig. 1 (Plate VII) shows photographs of typical specimens after thirty weeks' exposure in the accelerated test: all paint and corrosion products were removed before photographing. The mottled appearance of the specimens (*b*), which were exposed after chromating or etching but without painting, is due to superficial staining (especially of the pure aluminium *A*) and areas of very slight general corrosion which have been unavoidably exaggerated in the photograph. The D.T.D. 118 magnesium specimens have a rather mottled appearance owing to very slight irregularities in the initial appearance of the chromate film, which again have been exaggerated in the photograph. With all the specimens shown which had been painted with red lead primer (*e* and *n*), the attack consists mainly of pitting.

Steel specimens are still on test (p. 73) and hence could not be included in Fig. 1. In the accelerated test the steel specimens are in general much more severely corroded than the remaining (light alloy) specimens, with the exception of those painted with red lead primer.

2. *Industrial Station.*

Table IV gives a summary of the detailed results obtained at the industrial station after 25 weeks' exposure.

Red lead has caused some acceleration of the corrosion of light alloys, although the effect has not been so noticeable here as in the marine atmospheres. Nevertheless, severe local attack has been observed on the normal-purity magnesium alloys, the depth of attack being considerably greater than with the bare metal. With aluminium and B.S.S. 5L3, corrosion has been confined to the backs of the panels. The red lead and iron oxide primers have so far afforded protection to steel comparable with that given by the chromate primers, but this conclusion is based mainly on performance without top coats.

No high-purity-base magnesium alloys were exposed at the industrial station.

3. *Rural Station.*

Painted aluminium and B.S.S. 5L3 panels have so far shown no signs of failure, with the exception of the B.S.S. 5L3 specimens coated with a single coat of red lead primer, which show slight local corrosion on the panel backs only.

TABLE III.—*Summary of Results for Accelerated Test After 30 Weeks' Exposure.*

Paint System.	Main Paint Failures and Corrosion.						
	Pure aluminium (*A*).	B.S.S. 5L3 (*D*).	D.T.D. 120A, high purity (*Z*).	D.T.D. 118, normal purity (*Y*).	D.T.D. 59A, high purity (*W*).	D.T.D. 59A, normal purity (*V*).	Steel (*S*).
Zinc chromate primer (*c*).	None.	None.	Very slight local flaking.	Trace of local flaking.	Trace of flaking.	Moderate flaking and trace of local corrosion.	Slight flaking and slight local corrosion.
Zinc chromate primer + D.T.D. 63A top coat (*g*).	None.	None.	None.	None.	None.	Very slight flaking.	Very slight flaking at edges.
Zinc chromate primer + D.T.D. 260A top coat (*i*).	None.	None.	None.	None.	Trace of flaking.	None.	None.
Zinc tetroxychromate primer (*d*).	None.	None.	Slight flaking and trace of local attack at scratch and edges.	Trace of local corrosion.	Very slight local corrosion.	Very slight flaking and trace of local corrosion.	Considerable flaking and slight local corrosion.
Zinc tetroxychromate primer + D.T.D. 53A top coat (*h*).	None.	None.	None.	None.	Very slight flaking.	Trace of flaking at scratch.	Trace of blistering along the scratch.
Zinc tetroxychromate primer + D.T.D. 260A top coat (*m*).	None.	None.	None.	None.	None.	None.	Very slight blistering along the scratch.

Red lead primer (*e*).	Moderate paint failure and local corrosion.	Considerable paint failure and local corrosion at scratch and edges.	No paint remaining. Severe general corrosion.	No paint remaining. Severe general corrosion.	No paint remaining. Severe general corrosion.	No paint remaining. Severe general corrosion.	Severe paint failure and moderate general corrosion.
Red lead primer + D.T.D. 63A top coat (*j*).	Very slight paint failure and local corrosion.	Moderate paint failure and local corrosion at scratch and edges.	Severe paint failure and general corrosion.	No paint remaining. Severe general corrosion.	No paint remaining. Severe general corrosion.	No paint remaining. Severe general corrosion.	Slight blistering along the scratch.
Red lead primer + D.T.D. 260A top coat (*n*).	A trace of paint failure and local corrosion.	Slight paint failure and local corrosion at scratch and edges.	Considerable paint failure and general corrosion.	Very severe paint failure and severe general corrosion.	No paint remaining. Severe general corrosion.	No paint remaining. Severe general corrosion.	Very slight blistering along scratch.
Iron oxide primer (*f*).	None.	Trace of local corrosion.	Moderate flaking.	Very slight local failure and local corrosion.	None.	Slight flaking and local corrosion.	Moderate paint failure and general corrosion.
Iron oxide + D.T.D. 63A top coat (*k*).	None.	None.	None.	Trace of flaking.	Very slight flaking.	Slight flaking at scratch.	None.
Iron oxide + D.T.D. 260A top coat (*o*).	None.	None.	None.	Trace of flaking.	None.	Trace of flaking at scratch.	None.
Plain metal (untreated) (*a*).	Very slight general corrosion.	Slight general corrosion.	...	Slight local corrosion.	Very slight local corrosion.	Moderate local corrosion.	Considerable general corrosion.
Plain metal (chromated or pickled) (*b*).	Very slight general corrosion.	Slight general corrosion.	None.	Slight local corrosion.	Trace of local corrosion.	Slight local corrosion.	Considerable general corrosion.

TABLE IV.—*Summary of Results for Widnes (Industrial) Specimens After 25 Weeks' Exposure.*

Paint System.	Main Paint Failures and Corrosion.				
	Pure aluminium (*A*).	B.S.S. 5L3 (*D*).	D.T.D. 118, normal purity (*Y*).	D.T.D. 59A, normal purity (*V*).	Steel(*S*).
Zinc chromate primer.	None.	None.	Very slight local corrosion.	Very slight flaking. Slight local corrosion.	Slight flaking. Slight to moderate local corrosion.
Zinc chromate primer + D.T.D. 63A top coat	Moderate flaking of top coat on scratch lines only.	None.	None.	None.	Severe top coat flaking at scratch line only.
Zinc chromate primer + D.T.D. 260A top coat.	None.	None.	None.	None.	None.
Zinc tetroxychromate primer.	None.	None.	Very slight local corrosion.	Trace of local corrosion.	Slight local corrosion.
Zinc tetroxychromate primer + D.T.D. 63A top coat.	None.	None.	Slight to moderate scratch-line flaking of top coat.	None.	Severe top coat flaking at scratch line only.
Zinc tetroxychromate primer + D.T.D. 260A top coat.	None.	None.	None.	None.	None.
Red lead primer.	Slight local corrosion.	Slight local corrosion.	Severe local corrosion with resulting paint failure.	Severe local corrosion with resulting paint failure.	Slight local corrosion.
Red lead primer + D.T.D. 63A top coat.	None.	None.	None.	Severe scratch-line top coat flaking on one panel only.	Slight top coat flaking at scratch line.
Red lead primer + D.T.D. 260A top coat.	None.	None.	None.	None.	None.
Iron oxide primer.	None.	None.	None.	Slight local corrosion.	Slight local corrosion.
Iron oxide primer + D.T.D. 63A top coat.	None	None.	Slight to moderate scratch-line flaking of top coat.	None.	Slight top coat flaking at scratch line.
Iron oxide primer + D.T.D. 260A top coat.	None.	None.	Slight scratch-line flaking of top coat on one panel.	None.	None.
Plain metal (untreated).	Slight general corrosion.	Slight general corrosion.	Slight general corrosion.	Slight general corrosion.	Considerable general corrosion.
Plain metal (chromated or pickled).	Slight general corrosion.	Slight general corrosion.	Slight general corrosion.	Very slight general corrosion.	Considerable general

Single coats of red lead primer have produced severe local corrosion on the normal-purity wrought magnesium panels and very slight corrosion on the normal-purity cast magnesium alloy. No high-purity-base magnesium alloys were exposed at the rural station. Red lead primer so far compares favourably with other pigments on steel.

VI.—Discussion of Results.

The results show conclusively that red lead primers are unsuitable for light metals. The red lead has accelerated the corrosion of these metals, possibly by the deposition of metallic lead to form local couples which initiate corrosion of the more anodic light metals. The more anodic magnesium alloys show this effect more markedly than the other metals under test and suffer corrosion from this cause even in the rural atmosphere. The effect of the red lead becomes more marked as the corrosion conditions become more severe and as the purity of the base metal is lowered.

No acceleration of corrosion by painting has been observed with any of the other paint systems, and in fact, iron oxide has considerable merit as a priming pigment on light metals and is providing useful protection even in the more severe saline atmospheres.

The chromates appear to be the most successful primers for general use on all the light metals included in these tests, and so far corrosion has not been more than slight with either of the chromates, whether tested with or without top coats, on any of the metals, under the whole range of atmospheric conditions.

The general conclusions with respect to the materials tested are therefore that (1) red lead primers should not be used on light alloys; (2) both iron oxide and zinc chromate primers provide useful protection on both light alloys and steel; and (3) there is some indication that zinc chromates are superior to iron oxide on light alloys, but more prolonged exposure will be required to confirm this.

Acknowledgements.

The authors wish to express their appreciation of the advice and assistance received from Messrs. Cellon's, Limited, who made up the paints used and provided the data given in Table I and the Appendix. They also thank the Magnesium Metal Corporation for the preparation of the magnesium alloy specimens.

References.

1. H. A. Gardner, G. G. Sward, and L. P. Hart, *Nat. Paint, Varnish Lacquer Assoc. Circ.* No. **482**, 1935, 172.
2. F. A. Champion, *J. Inst. Metals*, **1943**, **69**, 47.

APPENDIX.

Further Details of Paints used in Tests.

1. *Primers.*—All four primers were formulated with a ratio of oil absorption of pigment to non-volatile of 0·66 : 1. The pigments used were :

	Oil Absorption (castor oil).
Turkey red oxide (B.S. 305 type 1a)	23·2%
Zinc chromate to D.T.D. 377A	35·0%
Non-setting red lead (B.S. 217)	7·5%
Zinc tetroxychromate (I.S.C., Ltd.)	54·0%

From these oil absorptions the formulæ were derived as follows :

Iron Oxide Primer.

Cerrux K4461	4 pints 6 fl. oz.
Dipentene	16 fl. oz.
Turkey red oxide	8 lb.
	6¼ pints

Red Lead Primer.

Cerrux K4461	4 pints 6 fl. oz.
Dipentene	16 fl. oz.
Red lead	24 lb. 13 oz.
	7½ pints

Zinc Chromate Primer.

Cerrux K4461	4 pints 6 fl. oz.
Dipentene	16 fl. oz.
Zinc chromate	5 lb. 5 oz.
	6 pints

Zinc Tetroxychromate Primer.

Cerrux K4461	4 pints 6 fl. oz.
Dipentene	16 fl. oz.
Zinc tetroxychromate	3 lb. 7 oz.
	5¼ pints

The varnish K 4461 had the following composition :

Linseed stand oil 40 poise	120 lb.
Cicoil (heat-treated oiticia oil)	120 lb.
Beckacite 1123	240 lb.
Cobalt naphthenate (6% Co)	2 lb.
Xylol	24 gal.
White spirit	24 gal.
	92 gal.

Beckacite 1123 is described as an esterified reduced phenolic resin.

Each primer was milled for 24 hr. in a 1-gal. Steele Cowlishaw porcelain pebble mill with constant speed and constant charge of porcelain pebbles.

2. *Top Coats.*—The aluminium finish for D.T.D. 63A was based on Noral paste, the vehicle consisting of nitrocellulose HL 30/40 (dry) 50%, non-drying alkyd resin 22%, and plasticizer 23% ; that for D.T.D. 260A was also made from Noral paste, the medium being a dilution of a medium length linseed oil modified alkyd resin (Paralac 16X).

THE DAMPING CAPACITY OF METALS IN TRANSVERSE VIBRATION.* 1144

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SYNOPSIS.

The development is described of a method for the measurement of damping capacity at low stresses on specimens of uniform cross-section vibrating transversely in the "free–free" mode.

The damping capacity of aluminium-rich alloys (R.R. 56, R.R. 88, and Duralumin) measured with the fully developed apparatus ranges between 0·0022 and 0·0035%. The discrepancy between these values and those published by Frommer and Murray (*J. Inst. Metals*, 1944, **70**, 1) for specimens of similar material in torsional vibration can be explained by the existence of transverse thermal currents in the former case.

The changes of damping capacity during the ageing of Duralumin and R.R. 56 at room temperatures following solution treating and quenching, were measured; in addition, it was found that a marked decrease in damping capacity resulted from precipitation at elevated temperatures in R.R. 56 and copper–beryllium which had previously been aged for over 18 months at room temperature.

I.—INTRODUCTION.

THE damping capacity of polycrystalline metals at low stress is independent of both the amplitude of vibration and the number of stress cycles. At any frequency, therefore, measurement under these conditions yields results which are uniquely determined by the metallurgical condition of the specimen, and provides a convenient and potentially valuable research technique in the field of physical metallurgy. In this connection, investigators have already obtained experimental evidence which shows that such factors as grain-size,[1] heat-treatment of steels,[2] order–disorder changes,[3] and cold work,[4] have a marked effect on the damping capacity of the material.

A necessary pre-requisite to any investigation of the relation between the condition of a metal and its damping capacity is the development of a reliable method of measurement. The difficulties encountered in this process are principally experimental, and arise from the low damping value characteristic of many metals at low stresses. For example, in the case of extruded Duralumin in torsional vibration, the damping capacity may have a value corresponding to an energy dissipation of 0·0012% of the vibrational energy per cycle.[5] Under these conditions, the magnitude of extraneous energy losses must be reduced to exceed-

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ingly small proportions in order to obtain a reliable indication of the energy loss produced solely by effects within the specimen. Careful design of the apparatus is therefore essential.

It is only in recent years that satisfactory measurement techniques have been developed. The work of Frommer and Murray,[5] using torsional vibrations in the frequency range 1–10 kc./s. is outstanding in this direction, and that of Zener and his collaborators has resulted in an equally loss-free method for longitudinal vibration. The latter is based on a design of Wegel and Walther,[6] and operates at frequencies above 5 kc./s.

The case of transverse vibration is rather different. As a result of a preliminary investigation, Frommer and Murray [5] concluded that apparatus losses are greatest in this type of vibration and likely to be the most difficult to eliminate; this led them to select torsional vibration for their work, since the losses are inherently smaller. The method developed by Förster [7] appears to give results higher than those characteristic of torsional and longitudinal vibration, while although Zener appears to have used a more loss-free method,[4] it has not been described in detail, and its application has been limited to α brass.

In this paper the development is described of a method for the measurement of damping capacity in transverse vibration. The main objects of the work were firstly to assess the magnitude of extraneous energy losses which arise, and secondly to obtain results which could be compared with those measured in torsional and longitudinal vibration.

Apparatus losses are more likely to be manifest when testing specimens of low damping capacity, and for this reason the work was carried out mainly with aluminium-rich alloys, which have been shown to have a very low damping capacity in torsional vibration.

The changes of damping capacity accompanying the ageing of Duralumin and R.R. 56 at room temperature were measured with the fully developed apparatus; and the effect of precipitation at elevated temperature in R.R. 56 and copper–beryllium was investigated.

II.—The Apparatus for the Measurement of Damping Capacity in Transverse Vibration.

1. *Principle.*

The damping capacity is derived from measurement of the rate of fall of the amplitude of vibration of a freely suspended specimen of uniform cross-section vibrating in the "free–free" mode. Vibrations are generated by feeding current from an electronic oscillator, at the natural frequency of vibration of the specimen, into an exciter unit

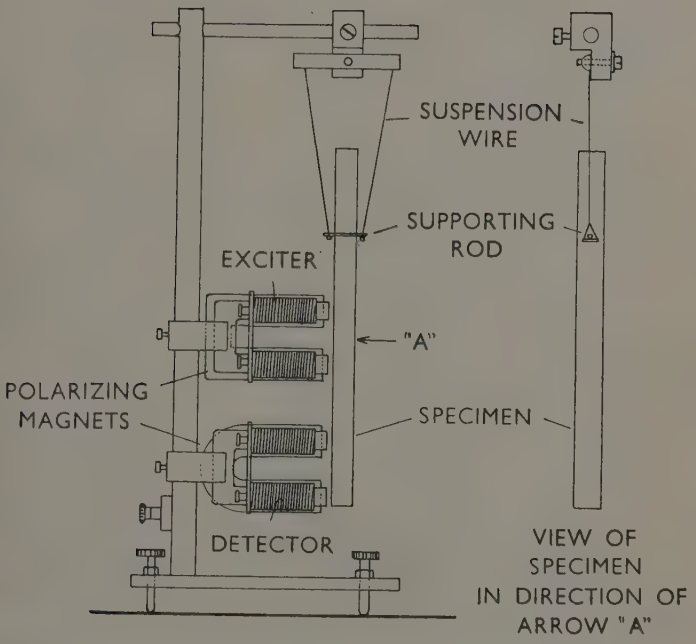

FIG. 1.—Diagram of Flexural Apparatus, Showing Suspension System and Exciter and Detector Units.

[*To face p.* 82.

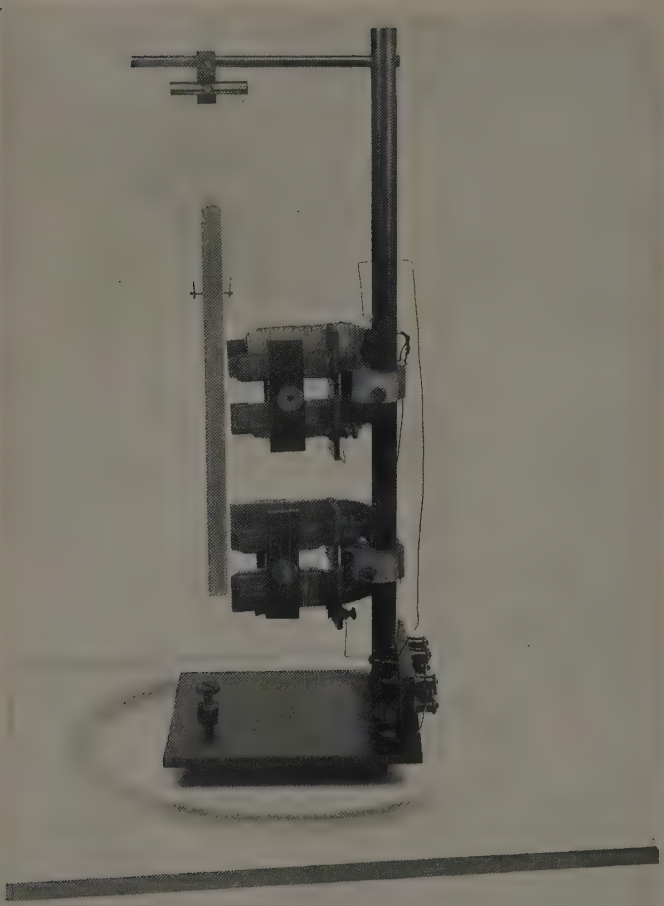

FIG. 2.—Photograph of Flexural Apparatus.

working on the well known principle of the interaction between a constant polarizing field and eddy currents generated in the metal by an alternating magnetic field. The decay of the amplitude of vibration following the removal of the exciting force is measured from the amplified voltage generated in a similar unit.

2. *Form of Specimen and Method of Suspension.*

In the development of a method of suspension, consideration was given to the fact that tests at reduced air pressures were contemplated, and an attempt was made to design an arrangement which could conveniently be enclosed in a bell-jar. For this purpose the specimen was drilled on the neutral axis of bending at a point corresponding to a node of vibration, and a $\frac{1}{16}$-in.-dia. hard-steel rod was pressed into the hole. The projecting ends of the rod rested on stirrups at the ends of two fine wires, and, in this manner, the specimen was suspended in a vertical position.

With this arrangement, suspension losses are likely to arise if the plane of vibration is not at right angles to the axis of the supporting rod. This condition may arise with specimens of square or circular section, since the slightest geometrical imperfection in the section results in the existence of two orthogonal planes of vibration, whose directions are governed by the asymmetry and bear no relation to that of the exciting force. Non-uniform density or elastic modulus over the section would have the same effect, but it is considered that geometrical asymmetry is the predominant factor in most cases.

An investigation of the planes of vibration of a specimen of R.R. 56 of ostensibly circular section 0·75 in. dia. was carried out while it was suspended in a horizontal position by two fine threads at the theoretical position of the nodes. The specimen was maintained in vibration while the end was illuminated and observed through a microscope. Two orthogonal planes of vibration were excited at frequencies of 1340 and 1340·3 c./s., respectively, and their directions were independent of the orientation of the exciter relative to the bar. This result could be explained by the existence of a slightly elliptical section, with a maximum variation in diameter of 0·00018 in.; no variation in diameter could be detected with a standard micrometer, outside the experimental uncertainty of the order of 0·0002 in. It is therefore difficult to determine the direction of the planes of vibration in this case by measurement of the specimen dimensions.

A specimen of square section was tested similarly, and orthogonal planes were observed making an angle of about 30° to the side of the section, their natural frequencies being separated by 1·6 c./s. The

geometrical asymmetry was in this case measurable, but was of such a complicated nature that no effort was made to relate it to the planes of vibration.

In an extruded brass bar the observed frequency difference between the planes of vibration, 2·08 c./s., was in fair agreement with the value of 1·85 c./s. calculated from the geometry of the section. The former frequency was determined acoustically. It is possible, with the planes of vibration each at about 45° to the exciter axis, to excite vibrations in both planes which co-exist for sufficient time as free vibrations for the beat frequency to be measured aurally.

These experiments confirmed that specimens of rectangular section would be the most satisfactory from the point of view of the envisaged method of suspension. In this case, the existence of slight asymmetry does not result in any marked displacement of the planes of vibration from directions parallel to the sides of the section. This has the advantage that the planes are pre-determined, and the drilling operation is easy since the hole is normal to the side of the specimen; in addition, the two frequencies may be widely separated, and the possibility of exciting the unwanted mode is rendered very remote. Specimens of circular section were used successfully by first determining the planes of vibration experimentally and drilling the hole for the supporting rod normal to one of them.

3. *Location of Nodes.*

An essential preliminary to the preparation of the specimens for suspension is the location of the nodes of vibration. All measurements were carried out at the fundamental natural frequency in the "free–free" mode, for which Rayleigh [8] has calculated the position of the nodes to be 0·224 of the length of the bar from each end. This treatment assumes that the length is large compared with the depth, and for this reason the applicability of this theoretical value to the size of specimen used in this apparatus was investigated experimentally.

Dry powdered glass was sprinkled on the upper surface of a bar of rectangular section suspended horizontally and excited into vibration at the maximum amplitude attainable. The powder was agitated into lines across the bar at the nodes within ½ mm. of the theoretical position. This result justified the procedure adopted in all the subsequent work of locating the supporting rod at the theoretical position of the node. The centre of the hole for the rod was displaced towards the end of the bar so that the supporting points would be exactly at the node.

Specimens of both rectangular and circular section, prepared and suspended in this manner, were observed microscopically during vibra-

tion, and in every case the plane of vibration was at right angles to the axis of the supporting rod.

4. *Details of Apparatus.*

The arrangement of the specimen suspension system, together with the vibration exciter and detector units, is shown in Fig. 1 (Plate VIII) and Fig. 2 (Plate IX). The hard-steel rod supporting the specimen rests on stirrups at the ends of two 0·005-in.-dia. copper–beryllium wires. These are soldered at their upper ends to a horizontal bar, which is pivoted at its mid-point so that any deviation of the specimen axis from a vertical position may be corrected by slight rotation. The suspension system is carried on a horizontal arm fixed to the vertical pillar carrying the exciter and detector units. The latter can be moved up and down the pillar, and this adjustment, together with levelling screws in the base and movement of the point of suspension along the horizontal arm, permits adequate variation of the relative disposition of the exciter, detector, and specimen.

5. *Electrical Equipment.*

Frommer and Murray [2] have pointed out the necessity in apparatus of this type for an oscillator of high frequency stability fitted with a fine frequency adjustment. This requirement is imposed by the sharpness of the amplitude–resonance curve for many metal specimens, and was adequately met in this apparatus by the use of a Muirhead decade-resistance-tuned oscillator, which had been fitted with an extra dial giving a continuously variable increment of frequency between 1 and 2 c./s. Power was fed from the oscillator to the exciter through a matching and power-factor correcting circuit.

The exciter polarizing field was supplied by an electromagnet so that the current supply could be interrupted during the decay of vibration in order to eliminate damping which would otherwise result from the generation of eddy currents.

The voltage generated in the detector was amplified and measured on a rectifier meter, a potentiometer between the first and second stages of the amplifier being used to vary the over-all voltage-amplification factor. Although the detector voltage is strictly proportioned to the velocity of the specimen, it may also be considered proportional to the amplitude, since all measurements are made at constant frequency and only amplitude ratios are involved.

A schematic diagram of the arrangement of the electrical apparatus is given in Fig. 3.

6. *Measurement of Damping Capacity.*

The results are all expressed in terms of the specific damping capacity P, defined by:

$$100 \times \frac{\text{vibrational energy lost during one cycle}}{\text{vibrational energy at beginning of the cycle}} \%,$$

where the instantaneous vibrational energy is the sum of the kinetic and elastic energies.

Measurement of the time taken for the amplitude to fall to half of its initial value, over a wide range of detector-voltage-amplification

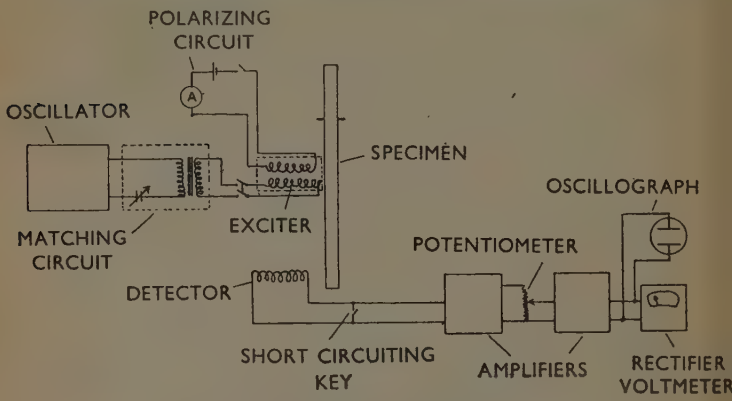

FIG. 3.—Schematic Diagram of Electrical Apparatus.

factors, showed that the half-amplitude time was constant for all the specimens tested in the amplitude range attainable. This indicates that the logarithmic decrement is independent of the amplitude of vibration, and the specific damping capacity may therefore be derived to a close approximation from:

$$P = \frac{200}{ft} \log_e 2\%,$$

where f is the frequency of vibration and t the half-amplitude time.

The value of P calculated by this expression exceeds the true value by about $\frac{P}{2}$ %, which, in these experiments, corresponds to a maximum error of 0·04%.

7. *Investigation of Apparatus Losses.*

Three possible sources of apparatus loss were investigated: (*a*) air loss; (*b*) suspension loss; (*c*) eddy-current damping generated by motion of the specimen in the detector polarizing field. In addition, the error introduced by the recording voltmeter was measured.

(*a*) *Air Loss.*

The contribution to the damping capacity arising from air friction and acoustic radiation was measured directly by carrying out tests at

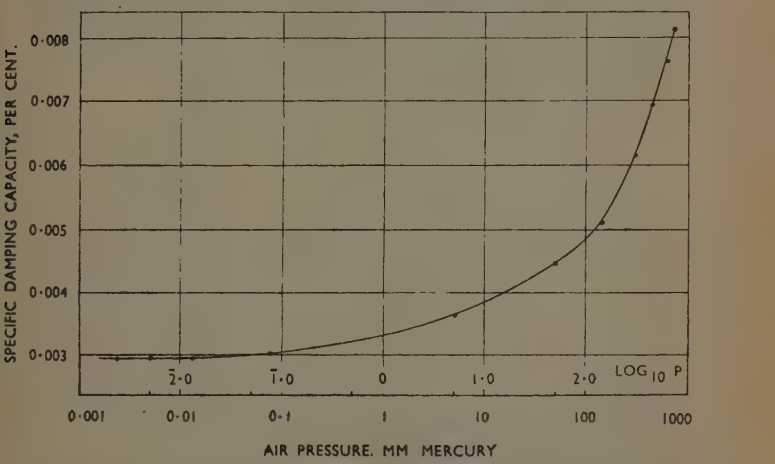

FIG. 4.—Variation of Damping Capacity with Air Pressure in Flexural Vibration. Specimen: R.R. 56, 0·7 in. dia., 10 in. long. Frequency of vibration: 1345 c./s. Measurements are not corrected for detector loss, which in this case is about 0·0003%.

reduced air pressures. For this purpose, the specimen and its supporting stand were placed on a sheet of plate glass and covered with a bell-jar. A rotary pump, supplemented when necessary by an oil diffusion pump, was used to evacuate the jar, and pressures below 0·1 mm. of mercury were measured with a McLeod gauge. Leads from the detector and exciter units were brought outside the bell-jar through three glass tubes passing through a rubber stopper in the opening at the top; the wires were sealed into the tubes with "Picine" wax.

The variation in measured damping capacity with air pressure for a fully heat-treated R.R. 56 specimen is shown in Fig. 4. The value decreased from $0{\cdot}011_2$ to 0·0082% when the bell-jar was placed over

the specimen without any pressure change; this is attributed to the formation of standing waves in the air between the specimen and jar surface. The reduction in the measured damping capacity to 0·0030% at the lowest pressures shows that an air loss exists which is in this case at least three times the specimen damping. It is inferred from Fig. 4 that the major part of the air loss is eliminated at a pressure of about 10^{-2} mm. of mercury. The damping capacity was found to be independent of the amplitude of vibration at all pressures.

Measurements at atmospheric pressure may give a false indication of the relative damping capacity of specimens of different form. Two specimens of R.R. 88, one of circular and the other rectangular section, were tested at both atmospheric pressure and 0·006 mm. of mercury with the results given in Table I.

TABLE I.

Specimen Size.	Frequency, c./s.	Atmospheric Pressure.		0·006 mm. Mercury.	
		Half-Amplitude Times, sec.*	P, %.	Half-Amplitude Times, sec.*	P, %.
0·6 in. dia. circular section	1726	7·6, 7·6, 7·6, 7·6, 7·4	0·0106	27·3, 27·3 27·5, 27·3, 27·6	$0·0029_4$
0·6 × 0·4 in. rectangular section	1974	5·4, 5·4, 5·4, 5·4	0·0130	25·7, 25·7	$0·0027_5$

* The values of the half-amplitude time were measured at different amplifier gains.

The difference in measured damping capacity is reduced from 0·0024 to 0·0002% by the elimination of air loss, showing that the discrepancy between the values at atmospheric pressure results from the higher air loss over the specimen of rectangular section.

The air loss for any specimen, when expressed as a specific damping capacity, will be dependent on such factors as its dimensions, frequency, surface finish, and physical properties. In general, factors which tend to increase the strain energy to surface area ratio (such as, for example, high density and elastic modulus) will decrease the air loss. This is illustrated by the result of the measurement of the air loss for a brass specimen of dimensions similar to that of the R.R. 88 bar of rectangular section referred to in Table I. The value was 0·0028%, i.e. about a quarter of that arising in the latter case. The modulus of elasticity of the brass is greater than that of the light alloy by about 50%, and the density is greater by a factor of three.

(*b*) *Suspension Loss.*

Errors in the location of the supporting rod may result in energy loss from the specimen through the suspension and at the points of support. An indication of the precision required in positioning the rod to avoid such errors was given by the following experiment:

A specimen of R.R. 56 of circular section and length 25·4 cm. was drilled at a node, suspended in the normal manner, and tested at low air pressure. The damping capacity was $0{\cdot}0027_6\%$. A hole was then drilled in a position 5 mm. from the other node and normal to the same plane of vibration, the damping capacity being unchanged. The supporting rod was then transferred to the second hole and the specimen re-suspended. The damping capacity in this condition was $0{\cdot}0027_0\%$. Subsequent results showed that the lower damping capacity in the second case resulted from a reduction of eddy-current loss arising from an increase in width of the detector air gap, and therefore that a 5-mm. displacement of the rod from the node introduces a suspension loss too small to be measured.

A similar test was carried out on a shorter specimen of Duralumin (20·0 cm.) with the supporting rod displaced 1 cm. from the node and its axis rotated through $14\frac{1}{2}^\circ$ relative to the normal to the plane of vibration. Even this degree of misplacement resulted in only a small increase in the measured damping capacity, from $0{\cdot}0027_0$ to $0{\cdot}0027_8\%$.

(*c*) *Damping Contributed by the Detector.*

A loss of vibrational energy of the specimen arises from the heat generated by eddy currents, which circulate in the end of the bar as a result of motion in the polarizing magnetic field. An attempt to measure this by the use of an optical method of amplitude measurement was unsuccessful, since it was found to be difficult to obtain high enough sensitivity.

The order of the energy loss was measured in the following manner. The damping contributed by the polarizing field of the exciter was derived from the difference between the half-amplitude times, measured firstly with the magnetic field maintained during the amplitude decay, and secondly with the energizing current switched off. The detector and exciter air gaps were equal in this test, and the procedure was repeated after the gaps had been increased by the same amount. It was assumed that the increase in air gaps would result in the same fractional reduction in the exciter and detector loss, since the two units are of similar dimensions and, under the conditions of this experiment, the energy loss is determined solely by the effective magnetic field

strength in the specimen. The derivation of the approximate detector loss from the results is given below :

Specimen : R.R. 56, 10 in. long × 0·6 in. dia.
Frequency : 1364 c./s. *Pressure :* 0·005 mm. mercury.

(i) Detector and exciter gaps 3·0 mm. wide.
Exciter polarized, $0{\cdot}0028_9\%$.
Exciter not polarized, $0{\cdot}0027_6\%$.
Exciter loss by difference, $0{\cdot}0001_3\%$.

(ii) Gaps both 1·0 mm. wide.
Exciter polarized, $0{\cdot}0032_0\%$.
Exciter not polarized, $0{\cdot}0029_2\%$.
Exciter loss by difference, $0{\cdot}0002_8\%$.
Change in detector loss resulting from decrease of air gap from 3·0 mm. to 1·0 mm. $= 0{\cdot}0029_2\% - 0{\cdot}0027_6\% = 0{\cdot}0001_6\%$.
Detector loss in experiment (i) by simple proportion

$$= 0{\cdot}0001_6 \times \frac{0{\cdot}0001_3}{0{\cdot}0002_8 - 0{\cdot}0001_3} = 0{\cdot}0001_4\%.$$

Although the result is approximate, the order of the error involved indicates that it is unnecessary to measure it with precision. In all the experiments, the order of the detector loss has been assumed equal to that of the exciter loss and derived from measurement of the latter. In no case did the value exceed 0·0003%; at lower frequencies, however, the loss increases as a result of the greater effective depth of penetration of the eddy currents, and may become serious.

(*d*) *Error Introduced by Recording Meter.*

The measured decay time exceeds the true value since the voltage recorded by the meter lags behind that applied to the amplifier input. It was established experimentally that the meter reading fell approximately exponentially from a full-scale deflection, following short-circuiting of the amplifier input, and that the error introduced could be eliminated by subtracting 0·3 sec. from the half-amplitude time.

8. *Measurement of Maximum Stress.*

The maximum stress attainable at atmospheric pressure was calculated for several specimens from the lateral deflection of the end of the bar, measured to 0·001 cm. with a travelling microscope. The method is not capable of high accuracy, but no attempt was made to refine the technique since the variation of damping capacity is slight within the range of stress attainable with the apparatus in its present form.

The maximum stress occurs in the outer fibres of the specimen at

the mid-point, and was calculated from β, the lateral deflection of the end from the equilibrium position, by the relation :

$$f = 4{\cdot}53\,\frac{E\beta d}{L^2},$$

where $2L$ is the length of the bar and $2d$ its depth.

Typical values measured at atmospheric pressure were 2900 lb./in.^{2} for Duralumin and 280 lb./in.^{2} for α brass. These figures will be increased by the elimination of air loss; in the case of Duralumin specimens, which commonly have an air loss five times the specimen damping, this could result in a stress increase by a factor of 2·2.

III.—Effect of Metallurgical Condition on the Damping Capacity.

It was concluded at this stage that the apparatus was capable of measuring the damping capacity arising solely from effects within the specimen, and the research was directed towards the effect of metallurgical condition. The alloys investigated were Hiduminium R.R. 56 Duralumin, and copper–beryllium.

1. *Ageing of Duralumin.*

Two specimens of Duralumin were prepared from the same length of material, and were solution treated together at 495° C. for 2 hr. Fig. 5 shows the variation of damping capacity of the first specimen following quenching in water at 13° C., together with the variation of hardness of the second, which was quenched at the same time. The tests were repeated with the same specimens after ageing had proceeded for 500 hr. No change of damping capacity resulted from continuous vibration for 10 min. at the maximum amplitude attained in the tests, from which it is inferred that the ageing process is unaffected by the vibrations associated with the measurements.

The high air loss from the specimen made it essential to make the damping measurements at low air pressure. The time taken to reduce the pressure in the apparatus after the specimen had been suspended under the bell-jar made it impossible to obtain reliable results immediately after quenching, but, in the second test, a value of $0{\cdot}0029_3\%$ was measured 13 min. after the quench. If this figure is corrected for the residual air loss at that stage, it is then equal to that of the first point on the curve (Fig. 5).

The following factors are common to both tests :

(*a*) A low and constant damping capacity for a period immediately after quenching (about 0·0022%).

(*b*) A similar maximum range of variation (about 0·0011%).

(*c*) An indication that the damping capacity is not stable even after 500 hr., showing that ageing is still proceeding.

(*d*) A maximum damping capacity after 24 hr. This peak occurs when the rate of change of hardness is greatest, and the width of the peak appears to be related to the maximum gradient of the hardness curve.

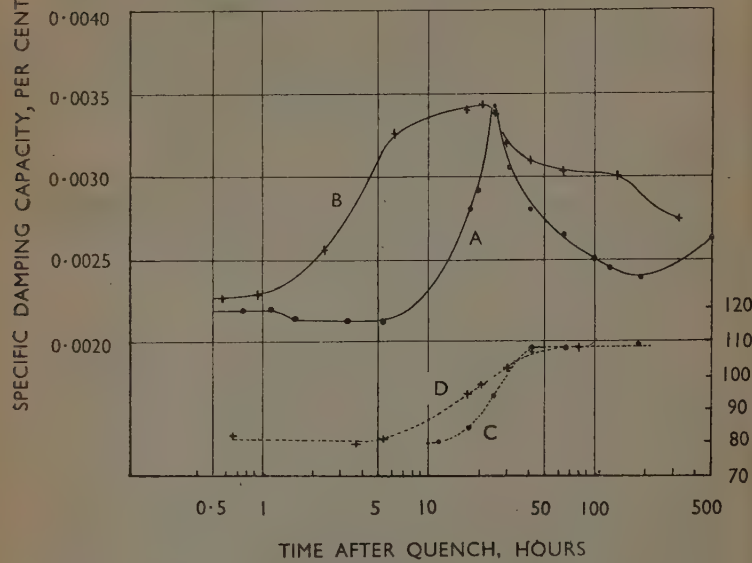

FIG. 5.—Ageing of Duralumin. Solution treated at 495° C. for 2 hr.; quenched in water at 13° C. Frequency of vibration: 2050–2057 c./s.

A. Damping capacity, first test. *C*. Vickers hardness, first test.
B. „ „ second test. *D*. „ „ second test.

2. *Tests on R.R.* 56.

Material was available in the form of $\frac{5}{8}$ in. square bars in both the solution-treated and fully heat-treated conditions, the former having aged at room temperature for 18 months. Two specimens of each of these were prepared, one of rectangular and the other of circular section, and were tested at both atmospheric pressure and 0·005 mm. of mercury. The results, corrected for all sources of error, are given in Table II.

TABLE II.

Condition.	Size.	P, %.		Corrected, P, %.	Frequency, c./s.
		Atmospheric Pressure.	0·005 mm. Mercury.		
Fully heat-treated	0·6 in. dia.	0·0127	$0·0036_7$	0·0034	1739
	0·625 in. × 0·314 in.	0·0135	$0·0040_7$	0·0038	2029
Solution treated and aged 18 months	0·6 in. dia.	0·0275	0·0188	0·0185	1725
	0·625 in. × 0·314 in.	0·0288	0·0188	0·0185	2058

The solution-treated specimens were then annealed at 169° C. for 10 hr. to bring them into the fully heat-treated condition. The damping capacity measured the following day was similar to the result of measurement 3 months later, given in Table III.

TABLE III.

Condition.	Size.	P, %.		Corrected, P, %.	Frequency, c./s.
		Atmospheric Pressure.	0·005 mm. Mercury.		
Fully heat-treated	0·6 in. dia.	0·0122	0·0033	0·0031	1756
	0·625 in. × 0·314 in.	0·0138	0·0030	0·0028	2087

A striking difference between the damping capacity in the solution-treated and fully heat-treated conditions is apparent, involving a factor of over 5.

The increase in frequency of about 1½% resulting from precipitation at an elevated temperature probably indicates an increase in the modulus of elasticity.

The test results for the solution-treated and quenched specimens were obtained about 18 months after heat-treatment. Ageing will have taken place over this period, the nature of which is indicated in Fig. 6, which shows the variation in damping capacity of the R.R. 56 specimen of rectangular section after solution treatment for 2 hr. at 530° C. and quenching in water at 13° C. The damping capacity has a low and constant value for 2 hr. after quenching and subsequently rises to a high value over a period of 10 days.

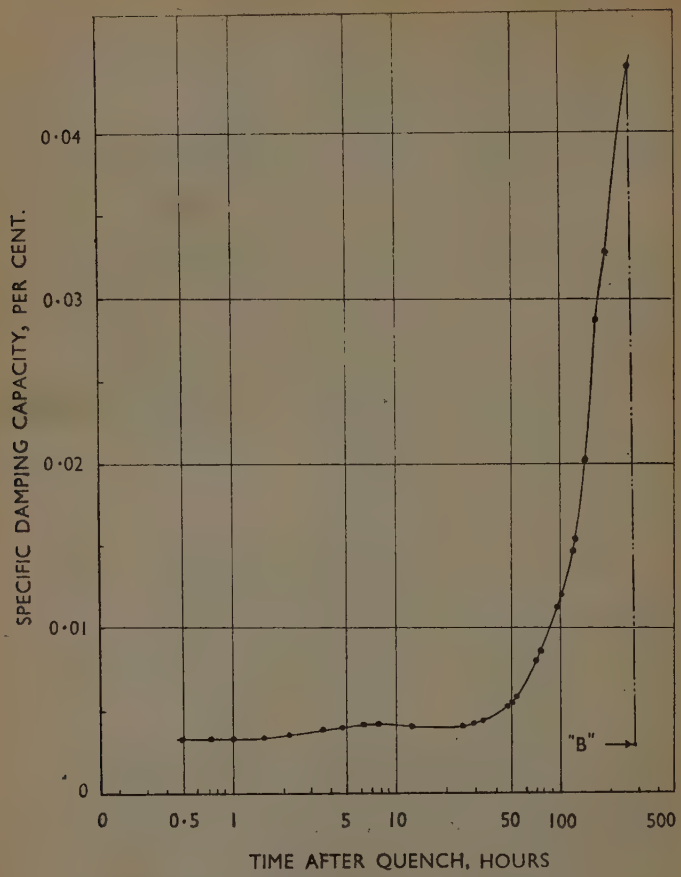

FIG. 6.—Ageing of R.R. 56 at Room Temperature. Solution treated 2 hr. at 530° C.; quenched in water at 13° C. Frequency of vibration: 2020–2029 c./s. "*B*"→ shows damping capacity following heating at 170° C. for 12 hr.

3. *Tests on a Copper–Beryllium Specimen.*

A single specimen of copper–beryllium of 0·6-in.-dia. section was prepared from material which had been solution treated and quenched 2 years before. The Vickers pyramid hardness of the specimen was 134, and its damping capacity, measured at an air pressure of 0·007 mm.

of mercury, was $0{\cdot}010_2\%$. The specimen was then heated for 2 hr. at 315° C., giving a hardness of 398 and a damping capacity of $0{\cdot}0025_7\%$. The decrease in damping was accompanied by an increase in frequency from 1284 to 1333 c./s.

The behaviour is thus qualitatively similar to that of R.R. 56.

IV.—Conclusions.

The most serious source of apparatus loss from freely suspended specimens in flexural vibration results from air friction and acoustic radiation, and is eliminated by conducting tests at pressures below 10^{-2} mm. of mercury.

A method of suspension using a rod pressed into a hole drilled at a node has been shown to introduce negligible energy loss. Specimens of rectangular section are most convenient, since their planes of vibration are parallel to the sides of the section, but specimens of circular section have been used successfully by determining their orthogonal planes of vibration experimentally and drilling the hole for the supporting rod normal to one of them.

The damping capacity of Duralumin measured with the fully developed apparatus varied between 0·0022 and 0·0030% at about 2000 c./s. This range is higher than that recorded by Frommer and Murray [5] for similar material, using torsional vibration (0·0012–0·0025%). Zener's theory,[9] however, predicts a contribution of about 0·0008% from transverse thermal currents in specimens of aluminium of dimensions and natural frequency similar to those of the Duralumin used in this work. On the assumption that the behaviour of Duralumin is similar in this respect to that of aluminium, the discrepancy between the results in torsional and transverse vibration is completely explained by the existence of transverse thermal currents in the latter case. It appears likely, therefore, that in this material the damping capacity resulting from all other causes is independent of the type of vibration. These conclusions are supported by a comparison between the results for R.R. 56 measured by Frommer and Murray, varying from 0·0020 to 0·0030% and those quoted herein, ranging from 0·0030 to 0·0038%.

Variations of damping capacity with changes in metallurgical condition have been recorded for precipitation-hardening alloys. In both Duralumin and R.R. 56 the damping capacity is lowest immediately after quenching from the solution-treating temperature. During the ageing of Duralumin at room temperature, the damping rises to a maximum after 24 hr. and subsequently falls to a value slightly higher

than that immediately after quenching. Under similar conditions, the damping capacity of R.R. 56 rises progressively over a period of 14 days to a value of 0·045%. Precipitation at 170° C. for 12 hr. produces a decrease in damping capacity to a stable value of about 0·003%. The behaviour of copper–beryllium is qualitatively similar in the latter respect, although the corresponding damping values are less.

Acknowledgements.

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THE EFFECT OF GRAIN-SIZE ON THE DAMPING CAPACITY OF ALPHA BRASS.* 1145

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SYNOPSIS.

The effect of grain-size on the damping capacity of α brass in both torsional and transverse vibration was investigated, using apparatus which has already been described (*J. Inst. Metals*, 1948, **74**, 373, and 1948, **75**, 81). The results are in close agreement with Zener's prediction of a contribution to damping capacity in all three kinds of vibration by intercrystalline thermal currents, which was verified experimentally in longitudinal vibration by Randall, Rose, and Zener (*Phys. Rev.*, 1939, [ii], **56**, 343).

I.—INTRODUCTION.

A COMPLETE explanation of the mechanism of the transformation of vibrational energy in metals has not yet been put forward. This results from two factors : the first is the comparatively recent development of reliable methods of measurement, and the second is the complex nature of the phenomenon, which, even in the simplest case of annealed, single-phase, non-ferromagnetic metals vibrating at low stress, appears to be the result of more than one effect.

Two significant contributions to the theory of damping capacity at low stress are those of Read and Zener.

The experimental work carried out by Read [1] on single crystals of zinc, copper, tin, and lead in longitudinal vibration indicated that an amplitude- and frequency-sensitive contribution arises, which he explained in terms of the movement of dislocations under the action of the alternating stress. This conclusion was supported by the effect of variation of the relative orientation of the slip planes and vibration axis. In polycrystalline specimens at low stresses, however, this contribution appears to be absent or at least very small, since the amplitude sensitivity required by the theory is not observed experimentally.

Zener's theory [2] is based on the thermo-elastic effect, by which the temperature of an isotropic material with a positive coefficient of thermal expansion falls uniformly when it is instantaneously stressed elastically in tension. The temperature change is dependent on the amount of elongation, and, in consequence, stress gradients produce temper-

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ature gradients which cause heat currents to flow between the regions of stress inhomogeneity. By this mechanism, therefore, some of the vibrational energy of the specimen will be converted irrecoverably into heat wherever stress gradients (other than pure shear) exist. In a similar manner the magneto-elastic effect results in additional contributions in ferromagnetic materials, arising from heat generated by eddy currents and magnetic hysteresis.

The thermo-elastic effect has important implications with regard to the variation of damping capacity with frequency. All contributions resulting from thermal currents are frequency sensitive, rising to a maximum value when the periodicity of the vibration approaches the relaxation time for heat flow by conduction between the regions of stress inhomogeneity.

From this point of view, the contribution which is most important results from intercrystalline thermal currents, which theoretically should arise in all types of vibration. Randall, Rose, and Zener [3] have obtained experimental verification of the existence of this source of energy loss in the case of α brass in longitudinal vibration. They made measurements on specimens of different grain-size at three frequencies and showed that the results were in complete accord with Zener's predictions.

In view of the important implications of the theory, the work to be described was undertaken in order to investigate experimentally the extent of the intercrystalline contribution in torsional and transverse vibration. Alpha brass was used in these experiments so that the results would be directly comparable to those in longitudinal vibration published by Randall, Rose, and Zener.

II.—Zener's Theory.

Two important sources of stress inhomogeneity in metals give rise to "macroscopic" and "microscopic" thermal currents respectively.[7, 8] The first results from stress gradients inherent in the form of stressing (other than pure shear), and the second arises from the anisotropic elastic properties of metal crystals which, together with even partial random orientation, produce stress differences between adjacent grains and therefore intercrystalline heat currents.

In transverse vibration, the macroscopic effect arises from the linear variation of stress across the section, and the contribution to the damping capacity by the thermal currents produced is given theoretically by:

$$P_T = 200\pi \cdot \frac{E_S - E_T}{E_S} \cdot \frac{ff_0}{f^2 + f_0^2} \%,$$

where E_T and E_S are respectively the isothermal and adiabatic elastic moduli measured along the axis of the specimen and f is the frequency of vibration. P_T reaches a maximum at a frequency f_0, which, for a specimen of rectangular section, is given by :

$$f_0 = \frac{\pi D}{2d^2},$$

where d is the depth of the specimen and D is the thermal diffusivity. The transverse loss is theoretically independent of the amplitude of vibration, as are all contributions from thermal currents.

Zener has stated [3] that "all types of elastic vibration in polycrystalline specimens are accompanied by stress inhomogeneities between adjacent crystallites". The microscopic contribution is to be expected, therefore, in all three types of vibration. A precise theoretical estimate of this intercrystalline loss is difficult, but its frequency behaviour is qualitatively similar to that of the macroscopic effect, rising to a maximum at a frequency given approximately by :

$$\frac{f_0 g^2}{D} = \frac{3\pi}{2},$$

where g is the grain-size. Hence f_0 is dependent on g, and the relation between damping capacity and grain-size at a constant frequency should also show a peak at a value which satisfies the above-quoted condition. The work to be described involves, in essence, the experimental determination of relations of this kind.

III.—Measurements in Torsional and Transverse Vibration.

The damping capacity of α-brass specimens of different grain-size was measured in transverse and torsional vibration at low stress, where the value is independent of amplitude. The torsional specimens were each tested at three different frequencies, the flexural specimens at only one frequency.

1. *Apparatus.*

The apparatus which was used has already been described. The three methods available, two for torsional vibration [4] and one for transverse vibration,[5] all involve measurement of the rate of decay of a free vibration.

The flexural apparatus tests freely suspended specimens of uniform rectangular section excited electromagnetically into vibration in the "free–free" mode.

Both torsional methods use a specimen of the form first adopted by Hanstock and Murray,[6] with a cylindrical test length and integral ends

of larger diameter. In the higher-frequency apparatus, the specimen is freely suspended by a fine wire and excited into vibration electromagnetically; a much lower frequency is attained using the second method, in which one end of the specimen is expanded into a chromium-plated wheel and the other is gripped in a similar manner in a plate bolted to a substantial concrete bed. Vibrations are induced in the latter case by deflecting the wheel statically and releasing it instantaneously. The amplitude is measured optically.

All measurements may be made at an air pressure of about 10^{-3} mm. of mercury to eliminate air losses.

2. *Dimensions of Specimens.*

It is desirable to establish experimental conditions in which all contributions arising from causes other than intercrystalline thermal currents are at a minimum. In torsional vibration, where the stress is pure shear, the macroscopic loss is absent; but in transverse vibration Zener, Otis, and Nuckolls [9] have shown experimentally that in copper, for example, it can represent the greatest contribution at room temperature to the damping capacity at low stress. The dimensions of the flexural specimens were therefore chosen so that transverse thermal currents would be small at the natural frequency of vibration. The final size was 8 in. long, with a rectangular section $0{\cdot}57 \times 0{\cdot}36$ in., having a natural frequency of 1260 c./s. This results in a calculated maximum macroscopic loss at 0·24 c./s. and a contribution to the damping capacity of 0·00041% at the natural frequency, which is not likely to obscure the intercrystalline effect and will be the same for all the specimens, since they are of similar dimensions.

The initial dimensions of the torsional specimens were calculated to give a natural frequency of 1260 c./s. when freely suspended. They comprised a cylindrical test length 6 in. long and 0·5 in. dia., with integral cylindrical ends 1·2 in. dia. and 1·0 in. long.

3. *Experimental Procedure.*

Six identical torsion specimens and six flexural specimens were machined from 2-in.-dia. bars of α brass.

A preliminary experiment established that an adequate range of grain-size could be obtained merely by annealing the material, in the condition in which it was received, at temperatures between 520° and 900° C. One torsional and one flexural specimen were annealed together to give approximately the same grain-size in each case. The scale which was produced on the specimens annealed in the higher temperature range was removed by pickling in dilute nitric acid.

Damping-capacity measurements before and after pickling on the slightly scaled specimens annealed at 520° C. gave identical results.

The flexural specimens were tested at one frequency only, namely 1260 c./s. The torsional specimens were first tested freely suspended at 1260 c./s.; the test-length diameter was then machined down from 0·5 to 0·3 in., and the ends were ground to the standard taper (1 in 50 on the diameter) which would allow the specimens to be expanded into the low-frequency apparatus for a test at 14·2 c./s. Prior to this test, the machined specimens were tested freely suspended at 540 c./s. In this manner, results were obtained on each specimen at three different frequencies.

Zener, Clarke, and Smith [10] have shown that cold working increases the damping capacity of α brass, but that the contribution is removed by annealing for a short time at 200° C. Since no measureable change in damping capacity resulted from annealing the machined torsional specimens at 200° C. for 30 min., it is inferred that the results do not include any contribution from cold working.

In the flexural tests and the two higher-frequency torsion tests, the damping capacity was independent of the amplitude of vibration within the stress range attainable—about 300 lb./in.^{2} The torsional apparatus which was used for the tests at 14·2 c./s., however, generally employs a maximum stress in excess of this value, since the method of amplitude measurement is less sensitive. As a result, the damping capacity was found to increase at the higher amplitudes by an amount dependent on the initial stress, indicating the presence of strain-hardening. Nevertheless, all the results showed a limited range at low stresses where the damping capacity was independent of the amplitude of vibration and unaffected by the initial stress. This value was selected as being representative of the contributions under investigation, and the initial angular strain in all the tests was kept below $2{\cdot}5 \times 10^{-4}$.

4. *Measurement of Grain-Size.*

The grain-size of the twelve specimens was determined by the method suggested by Jeffries and Archer.[11] An image of the micro-section was projected on a screen, and the magnification adjusted so that, where possible, at least 50 grains were enclosed by a circle drawn on it. The number of grains effectively enclosed was derived from the sum of those completely inside the circle and half of those intersected by it. The grain-size was expressed as the square root of the average grain area.

A variation of grain-size of almost 20% existed over the section of some of the flexural specimens, and as a result, the mean value of determinations at nine different points was recorded. The torsional

specimens showed less variation, and the values quoted are the mean of three determinations in each case.

The average number of twins per grain was obtained by dividing the number of twin bands intersected by a diametral line to the circle on the screen by the number of grains intersected. Table I gives the grain-size results.

TABLE I.—*Results of Grain-Size Measurements.*

(a) *Flexural Specimens.*

Diameter of field of view: 7·75 cm.

Specimen No.	Annealing Temp., °C.	Average Number of Grains (mean of 9 readings).	Magnification, dia.	Average Grain-Size, mm.	Twins per Grain.
2	900°	46	11	0·92	2·24
6	840°	64	20	0·41	2·15
5	770°	98	30	0·24	2·0
3	680°	66	72	0·13	1·8
4	600°	134	100	0·059	1·6
1	520°	96	200	0·034	1·9

(b) *Torsional Specimens.*

Diameter of field of view: 7·5 cm.

Specimen No.	Annealing Temp., °C.	Average Number of Grains (mean of 3 readings).	Magnification, dia.	Average Grain-Size, mm.	Twins per Grain.
2	900°	19·5	20	0·75	2·1
6	840°	84	20	0·36	2·1
5	770°	72·5	50	0·16	2·1
3	680°	92·5	50	0·14	1·87
4	600°	110	100	0·063	1·87
1	520°	149	100	0·054	1·9

IV.—Discussion of Results.

The experimental results are shown in Fig. 1, each curve representing the variation of damping capacity with grain-size at a constant frequency. They afford experimental support for the existence of a contribution to damping capacity in torsional and transverse vibration by intercrystalline thermal currents. The peak in the curve for transverse vibration at a grain-size of 0·33 mm. compares well with the approximate theoretical value of $\sqrt{\frac{3\pi}{2} \cdot \frac{D}{f_0}}$, which, at 1260 c./s. with $D = 0{\cdot}33$ cm.^{2}/sec., is 0·35 mm. If the same law of variation exists in torsional vibration, peaks would be expected at 0·35, 0·55, and 3·3 mm.

for frequencies of 1260, 540, and 14·2 c./s., respectively. The experimental values are 0·33 and 0·52 mm. in the first two cases, and, although the range of grain-size does not extend to a value high enough to include the peak of the 14·2-c./s. curve, the trend of the upper part is consistent with a peak at about 3·3 mm.

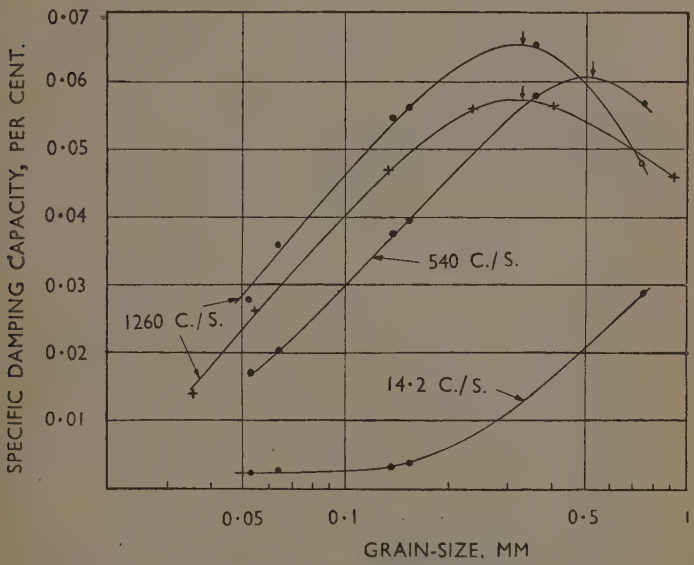

FIG. 1.—Effect of Grain-Size on the Damping Capacity of α Brass.

Torsional vibration ●——●
Flexural ,, +——+

Vertical arrows show grain-size at which contribution from intercrystalline thermal currents is theoretically a maximum.

The maximum value of the damping capacity in the three cases where the peak was attained experimentally has the same order, namely 0·066, 0·061, and 0·058%, indicating that the maximum contribution from intercrystalline thermal currents is of the same order in torsional and transverse vibration. A comparison between these and Zener's results [3] for longitudinal vibration, with a maximum value of 0·058%, shows that the contribution has a similar value for all three types of vibration. This comparison would presumably require modification, however, if differences in preferred orientation existed, since this factor

affects the magnitude of the intercrystalline loss. In the extreme case of completely uniform orientation, for example, the intercrystalline loss would be absent.

In Fig. 2 all the experimental results, together with those of Randall, Rose, and Zener, are plotted against the dimensionless parameter $\frac{fg^2}{D}$. The points for torsional and flexural vibration fall on a single curve,

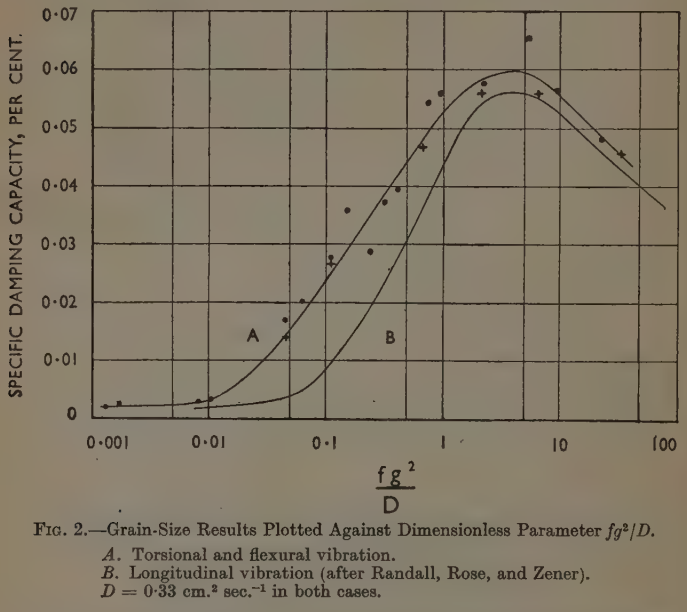

FIG. 2.—Grain-Size Results Plotted Against Dimensionless Parameter fg^2/D.
A. Torsional and flexural vibration.
B. Longitudinal vibration (after Randall, Rose, and Zener).
$D = 0{\cdot}33$ cm.^{2} sec.$^{-1}$ in both cases.

showing that the magnitude of the contribution is uniquely determined by the value of $\frac{fg^2}{D}$ in both types of vibration. The discrepancy between these results and those in longitudinal vibration appears to increase as $\frac{fg^2}{D}$ decreases. This cannot be the result of differing degrees of twinning in the two cases for, although measurements showed that such a difference did exist, the number of twins per grain was generally lower in the longitudinal case; thus an even greater discrepancy would be apparent were the $\frac{fg^2}{D}$ values based on the average twin dimension. It may be

that the discrepancy results from different grain-size distributions in the two cases.

This experimental identification of intercrystalline thermal currents in all types of vibration leads to the conclusion that a variation of damping capacity with frequency is to be expected in torsional, longitudinal, and flexural vibration. The magnitude of the variation will depend on the degree of elastic anisotropy and preferred orientation, and will be most marked when the frequency of vibration approaches a value corresponding to the relaxation time for heat flow between adjacent grains. If the vibrations can be considered either isothermal or adiabatic, the variation will be slight. This may account for the fact that Frommer and Murray [12] detected no variation with frequency in the damping capacity of aluminium-rich alloys in torsional vibration. The frequency range, 1–10 kc./s., together with large grain-size, make the conditions of vibration adiabatic; in addition, these alloys have a low elastic anisotropy.

It is of interest to compare the value for the damping capacity of α brass under isothermal conditions in all types of vibration. The value recorded here for torsional vibration (0·002%) is of a similar low order to that in longitudinal vibration (0·0019%) [3] and transverse vibration (0·0022%),[10] showing that the residual contribution to the damping capacity not explained by intercrystalline thermal currents is independent of the type of vibration. The lowest value measured for a single crystal of α brass in longitudinal vibration at 9 kc./s. is about 0·0019%.[13]

Since the maximum contribution from intercrystalline thermal currents is similar in all types of vibration, then, at any rate for annealed, single-phase, non-magnetic metals, the principal factor which will cause the damping capacity at low stress to be dependent on the kind of vibration is the macroscopic effect. This will result in a higher damping in transverse vibration at low frequencies, and a higher damping in longitudinal vibration at very high frequencies.

Acknowledgements.

The author wishes to thank the British Non-Ferrous Metals Research Association, which supplied the material for the specimens used in this investigation and has shown unfailing interest in the work. He acknowledges with gratitude the encouragement which he has received from Professor F. C. Thompson, D.Met., M.Sc., throughout the course of this research.

Mr. M. G. Cockcroft, B.Sc., assisted by carrying out the low-frequency torsion tests, and this help is much appreciated.

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AUTUMN LECTURE, 1948. 1146

THE CAVENDISH LABORATORY.

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NINETEENTH AUTUMN LECTURE TO THE INSTITUTE OF METALS, DELIVERED 16 SEPTEMBER 1948.

Synopsis.

A short description is given of the organization and work of the Cavendish Laboratory. The work is divided among separate groups who study nuclear physics, radio, low-temperature physics, crystallography, metal physics, and mathematical physics. Each group is largely self-governing and has its own workshop, store, and assistant staff. In addition there is a central store and workshop, a special-techniques section, and an electronics section for the design of special apparatus. The large and elaborate equipment required for research in nuclear physics necessitates the employment of special technical officers to run it. There are about 160 active research workers in the Department, drawn partly from the Honours courses given in the same laboratory, and partly from overseas. The work of organization is such that it occupies a full-time secretary in addition to the lecturing and research staff.

An account is given in outline of the research work being done by the different groups.

My warmest thanks are due to you for the compliment you have paid me in kindly inviting me to give your Annual Autumn Lecture. When I received the invitation I consulted your President, Sir Arthur Smout, and he encouraged me to think that a talk about the organization and work of the Cavendish Laboratory would be of interest to the members who are attending this meeting. I shall make it my aim, therefore, to describe how we have tried to set our house in order after the upheaval created by the war, and to give an account of the main lines of research which are going on in the Laboratory at the present time.

A major problem with which all scientific laboratories are faced is created by the great increase in the number of science students. In general, the numbers in the Universities in this country have about doubled, and in particular the proportion of physics students has increased in comparison with that of other students taking science, so that physics laboratories have had to expand their facilities for teaching

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and research very considerably above what had been provided in pre-war years. Specialized work in physics is carried out in our final Honours class, and it is this class which provides the recruits for research. Last year the number in this class was nearly three times the average figure of 40 before the war. The increase in the number of research students is quite as striking, and presents even greater problems, because physics research students require so much space and apparatus. We have at present, including the staff, some 160 people doing active research in the Laboratory. Part of this increase may be temporary, because the classes are swollen by men returning from the war, but there is no doubt that there will also be a very considerable permanent increase. Its extent depends on the national policy of financing University students for undergraduate studies and research.

These increases involve new problems of organization, and have led to a quantitative as well as a qualitative difference in the structure of the Laboratory. They necessitate a good deal of devolution of responsibility and lengthening of the lines of communication between the head of the Department and his students. It has interested me to try and assess how many men any leader can look after in a direct personal way, and I have arrived at a figure of five or six. For instance, one can look after half a dozen research students and have the necessary two- or three-hour talks with them at fairly frequent intervals that enable one to keep in close contact with the work and to guide them in prosecuting it. I can remember the early days when five or six research students was a common number in a laboratory, so that the head of the Department knew his researchers intimately, just as he knew as individuals the members of his small Honours class. I have seen the researchers grow to 5 or 6 squared and now they are 5 or 6 cubed. The organization of research work therefore involves dividing the men into large groups under leaders, and these large groups into smaller groups, so that the head of the Department is two removes from the researcher himself. Except in a few special cases of work in which he is particularly interested, he cannot have that close contact with the researcher which is essential for real direction.

The major groups in the Cavendish Laboratory are nuclear physics, radio, low-temperature physics, crystallography, metal physics, and mathematical physics. In addition, we have leaders in certain borderline subjects, who may not work wholly in the Cavendish, but who are, as it were, honorary members of our mess. For instance, we run the electron-microscope service for the whole University; Professor Sir Geoffrey Taylor carries out his work on turbulence in the Cavendish; we have under Sutherland one of the leading centres of infra-red

spectroscopy in this country; and we also have close relations with the work on geophysics and atmospheric physics in Cambridge.

The diversity of subjects represented by the research work is part of a deliberate policy. We have not only to provide for our own undergraduates who come on to do research, but also for many men from the Dominions and Colonies and from other countries who wish to do research in physics in Cambridge at the Cavendish Laboratory. It is very important that we should be able to give them a wide choice of subjects in which to carry out their research. We have tried in particular to keep the right proportion between the two great branches into which physics is conveniently divided at the present time, nuclear and cosmic rays on the one hand, and the rest of physics on the other. At the beginning of this century one could not have drawn a clear dividing line, but it is now becoming much more defined. There is the physics which deals with the ultimate particles of which matter is made and probes ever more deeply into their nature, and there is the physics which, as it were, starts with the properties of atoms and then tries to explain the richly diverse nature of the world which surrounds us and the properties of the materials which we encounter in every-day life. If we call the first cosmic physics and the second terrestrial physics we shall not be far wrong. Ours is a pleasant and tranquil world, in which easily understood laws like Newton's mechanics and the quantum theory apply, "good enough", as Dirac once said, "for most physicists and for all chemists". Laws far more difficult to understand govern the cosmic inferno of the universe, minute bits of which we copy in the huge machines of nuclear physics, or examine as they come to us from out of space as cosmic rays. Both these sides of physics have their own particular fascination and importance, and in the full training of a University physicist the study of both must have its place.

Each of the groups in the Laboratory is largely self-governing. When we know at the beginning of each year what sum of money our pleadings have managed to secure from the University, we make a rough division of the booty, and each group has its own order-book and buys its apparatus and supplies within the limit of its grant, except in the case of really major items of expenditure. Each group has its own workshop and a proportion of the assistant staff which works almost entirely within it. It has its own secretary, a most important individual nowadays when paper-work assumes such amazing proportions. It runs its own colloquium, a regular weekly meeting when papers by workers in other parts of the world are discussed and researchers give an account of what they are doing. As regards research, therefore, the groups are almost entirely independent. The teaching, on the other hand, is organized

centrally, everybody making his special contribution towards giving a well rounded lecture syllabus.

There are certain activities of the Laboratory which it is convenient to organize centrally. A new departure for us is our Laboratory secretary, a post which the University agreed to create some three years ago. The amount of administrative work, largely of a routine character, has greatly increased. This officer has in his charge finance, appointments of assistant staff and rates of pay, the formal work concerned with the admission of students, structural alterations and upkeep of the buildings, the preparation of agenda for meetings, and other duties of this nature. The appointment of an expert who can look after these matters and relieve the teaching staff of so much administrative responsibility has meant a great deal in the smooth running of the Laboratory. The central workshop service is common to all groups, where constructional work involving special machines is carried out. We regard it as most essential, however, that each group should have its own workshop for ordinary every-day constructional work. People who are born planners often attack us because of the supposed wastefulness of such a system, which leads to there being in all some nine workshops in the Laboratory, each with its own equipment, milling machines, lathes, drills, &c., but I am sure they are wrong. Research is not like production. The men are always altering their apparatus and trying out new schemes, and it is essential that they should have close personal contact with some mechanic who can often find odd bits and pieces to rig up a gadget with which they can try out some new idea. The opposite extreme of asking them to make a drawing which is then sent to a central workshop and put on a priority list would be quite fatal, and in the long run thoroughly inefficient. We have, of course, a central store and a central glass-blowing workshop. We have another central workshop which we call the "students' and boys'", where the researchers can embark on the more ambitious bits of construction without using the tools of the expert mechanics, an unthinkable proceeding, and where the youths joining the assistant staff can be trained.

In addition we have two units which deserve special mention. One which I always find rather fascinating is the special-techniques workshop, which roughly speaking is a place where all the jobs are done which nobody else can do, such as special glass-to-metal seals, very fine windows or small-scale gratings, evaporation of thin metal films, or construction and filling of Geiger counters with purified gases. These are only examples. I regard the special-techniques workshop as a kind of library of dodges; any one of us who hears about some special device, of whatever nature, files it there, so to speak, for future reference.

Another special unit is the electronics workshop for making amplifiers, counters, and other complex circuits involving thermionic valves and similar gear. The amount of equipment of this kind in a modern physics laboratory is very large, and it pays to have an expert in charge of such a unit and to give him the rather special types of tools required.

This will perhaps give you a general idea of the organization of the Laboratory, and I would now like to take you a somewhat breathless journey round it; it will be breathless because there is so much ground to cover, and I can only touch very lightly on the main features of the work going on in each group.

I cannot speak as an expert about the nuclear work. I am pre-eminently a terrestrial physicist, interested in the properties of matter rather than those of fundamental particles. I may touch lightly, however, on the peculiar problems which nuclear physics presents. It would seem that the more minute the particle we want to study the larger the apparatus which has to be built in order to do it. The scale of nuclear-physics apparatus is of quite a different order to anything which we needed before in the world of physics. We have not in Cambridge gear of the size which has been constructed in America, the great machines required to produce the particles of enormous energy which enable experiments simulating cosmic conditions to be carried out. We have nothing like Lawrence's cyclotron, which needs an army of several hundred skilled scientists and technicians to maintain it in running order and analyse the results which it produces, but even the scale of that which we have raises new problems of organization and administration. For instance, it does not pay to ask the research students to look after the apparatus themselves; it is too complicated and temperamental, and takes up too much time which they ought to be devoting to thinking of scientific questions and not of engineering ones. We have therefore had to create a new type of post, one for a technical engineer whose interest is in seeing that the gear works and not in the results which it produces. Much valuable time of researchers was wasted until this need was clearly seen and means were taken to provide for it. The machines we have as yet rise to no spectacularly high voltages. We have a small but reliable cyclotron, a very faithful million-volt set which has provided work for many research students, and a van der Graaf for $4\frac{1}{2}$ million volts is just going up and ought to be working soon; a project for a linear accelerator to go up to voltages of 100 millions is now in a very early stage. This side of the Laboratory is under the direction of Professor Frisch, who played so great a part in the development of nuclear energy during the war and who has recently come from Harwell to join our staff.

The radio section in the Laboratory is a legacy to us from Sir Edward Appleton, who was a Professor in the Cavendish when I came to it in 1938. We can claim it to be an outstanding centre of research in this country on the propagation of radio waves, study of the ionosphere, and recently the study of the radio waves which reach us from cosmic sources. It is at present under the charge of Ratcliffe, who is specially interested in the structure of the lower ionosphere and the propagation of long waves. The work on the radio waves coming from sun-spots and from other centres in the sky is carried out by Ryle, and represents a fascinating new kind of astro-physics. We are getting information about the universe around us not by light waves, which were previously our only messengers, but by waves in the radio region, and the work is writing a new chapter in astro-physics.

The Mond Laboratory, directed by Shoenberg, is concerned with work at very low temperatures and is one of the few centres in this country where liquid helium is regularly produced and used for experimental work. Liquid helium is a starting point for all work in the region within only a degree or so of absolute zero. The importance of investigations at this temperature is that the atoms have been robbed of almost all their thermal motion. In consequence a whole new range of physical properties can be studied, which is obscured by the irregular motion of the atoms at higher temperatures. Just as the anxious photographer tells his audience to keep quite still while he takes the cap off his camera, so the physicist likes the atoms to keep quiet while trying to discover some of their more delicate and small-scale properties. By the magnetic method of cooling, temperatures of within 1/100th of a degree of the absolute zero can be attained, and we have the apparatus for carrying this out.

The department which we call " crystallography " would perhaps be better described as the department for discovery of the structure of the solid state. This is the field in which I have done most of my scientific work, and I am fortunate in having one of the leaders in it, Taylor, to run the laboratory. Mainly by X-ray analysis we seek to discover the way the atoms are arranged in crystals and in other forms of solids. The scope of the work is very considerable. At one end we are investigating such substances as minerals and alloys in the inorganic field; other researchers are examining complex organic compounds in collaboration with Professor Todd in the Department of Chemistry; finally, at the other extreme we have a little group which is financed by the Medical Research Council under the direction of Perutz, which is engaged in a gallant attempt to work out the structure of the highly complex molecules which build up living matter, the proteins. These

giant molecules, which contain thousands of atoms, are far more complex than anything as yet analysed by X-rays, and we are only beginning to get a very rough idea of their structure. It is an exciting field, however, because the prize to be won is so great if we are successful. It would open up a new chapter in science if one could get an idea of the structure and functioning of these very complicated molecules.

This section of the Laboratory is closely linked to metal physics, under Orowan. His students are particularly studying the mechanical properties of metals and relating them to their structure. The effects of cold work on a metal, recrystallization, the yield point and plastic flow, brittle fracture, distortion under rolling or drawing, and so on, are being investigated as physical phenomena. A satisfactory theory of the strength of a metal has yet to be formed. We work in close collaboration with Mott's laboratory at Bristol and with Hanson and Raynor at Birmingham, two centres in this country which are particularly interested in metal physics.

Finally, we have an electron-microscope section under Cosslett which serves the whole University. Our country has fallen behind in the development of the electron microscope; it is not our fault, because the importance and usefulness of this type of microscope was just becoming recognized when the war started, and other countries developed it when all our efforts were going into war work. It is clear now, however, that it is one of the great tools of science, and we must make good our late start. We have got two electron microscopes of a commercial type. On the one hand Cosslett is trying to improve their performance, on the other to develop new methods of the preparation of specimens which will help researchers to use the microscope as a tool. Most of the work is done for the biology departments in the University, which have been very appreciative of its services. A Summer School for users of the electron microscope all over the country has been organized this year in the Laboratory. The Electron Microscopy Group of the Institute of Physics, of which Cosslett is Secretary, held its annual meeting in Cambridge, and we had many visitors from abroad.

I feel that in giving you an account of the work going on in the Laboratory I am giving you an account of our stewardship. We University teachers are privileged people because we are given freedom to research in the subjects which most interest us, and we are supported to do these researches by the industry of the country as a whole, using the word industry in its widest sense. This thought is always present in my mind when people talk of the debt which industry owes to science; I see the debt on the other side as well. We hear much of science in industry at the present time, a good deal of it of a rather facile and

not very profound kind. People talk as if science were a cure-all for industrial ills, and that if the patient does not seem to recover quickly all that is needed is to double the dose. It seems to me that as regards the development of new industrial successes, the hard tip to the tool which cuts into virgin material is not science. It ought more properly to be called invention, an imaginative act of thinking of something new made possible by an intimate knowledge of the conditions of industry, former achievements, needs, costs, practicability, and many other factors. Science is rather the support to the cutting edge of the tool, more than ever so nowadays. That support is given by the facts that science has discovered and the order to which it has reduced natural phenomena. It is for us in the Universities to find out this new knowledge, to teach it, and to put it in a form in which it is easily assimilated by those who wish to use it. My theme to-night has been the way in which we are trying to do our part of a joint task.

THE CONSTITUTION OF TIN-RICH TIN–ANTIMONY–COPPER ALLOYS.*

By J. V. HARDING,† B.Sc., Ph.D., MEMBER, and W. T. PELL-WALPOLE,‡ D.Sc., MEMBER.

SYNOPSIS.

The constitution of tin-rich alloys containing up to 14% antimony with 3% copper has been determined by thermal and microscopical analysis. The phases found are similar to those of the binary systems, namely α tin-rich solid solution, β (SbSn), and γ (Cu_6Sn_5): the liquidus consists of three areas corresponding to the primary separation of these phases.

The temperature of the peritectic reaction β + liq. $\rightarrow \alpha$ of the antimony–tin system is depressed by the addition of copper, and the eutectic of the copper–tin system liq. $\rightarrow \alpha + \gamma$ is raised by the addition of antimony. A ternary reaction β + liq. $\rightarrow \alpha + \gamma$ occurs at 239·5° C., the liquid phase containing 7·6% antimony with 0·97% copper.

The constitution in the solid state has been determined by microscopical examination of annealed alloys. The most important feature is the solid solubility of antimony, which decreases from ~9% at the solidus to ~2·5% at 20° C. In chill-cast alloys, a supersaturated α solid solution is retained containing ~7% antimony.

The structures and applications of typical cast bearing alloys of this system are correlated with the features of the equilibrium diagram.

I.—INTRODUCTION.

ALTHOUGH tin-base alloys with copper and antimony have been used as bearing metals for over a century, there is little published work on their constitution in the solid state.

Bonsack [1] examined the structures of cast alloys. He found no ternary intermediate phases, and indicated that solid alloys in the tin-rich corner were contained by the triangle tin–CuSn–SbSn. Thermal analyses indicated a ternary eutectic at the same temperature as the tin–copper eutectic (given as 229° C.). Tasaki [2] also investigated the entire ternary system. By thermal analysis on alloys of rather widely spaced composition he constructed a satisfactory qualitative model of the system. In the tin-rich corner, he found an invariant reaction at 242° C. between liquid, CuSn, SbSn, and tin-rich solid solution, but did not give the compositions of the phases involved nor the equilibrium relations in the solid state. Ellis and Karelitz [3] studied tin-rich alloys only, and determined liquidus and solidus surfaces. For all alloys containing up to 12% copper and 12% antimony, they reported a

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solidus temperature of 225° C., which was identical with the temperature they found for the tin–copper eutectic and indicated the presence of this eutectic in a metastable condition, in the ternary alloys. The investigation described here, which was carried out in 1938–1940, covers the alloys containing up to 14% antimony and 3% copper.

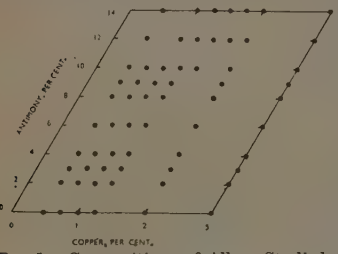


FIG. 1.—Compositions of Alloys Studied.

Fifty-seven ternary and six binary copper–tin alloys (Fig. 1) were examined, but no tin–antimony binary alloys were prepared, since a satisfactory account of the relevant part of the system has been published [4] (Fig. 2). Further, the solid solubility of copper in tin has been shown to be extremely small,[5, 6] and therefore no attempt has been made in this investigation to determine its solubility in the ternary alloys.

II.—Experimental Details.

Alloys were prepared from 99·99% Chempur tin, 99·9% pure copper, and 99·7% pure antimony. The tin was melted under charcoal, and the additions made as temper alloys containing 50% antimony and 10% copper, respectively.

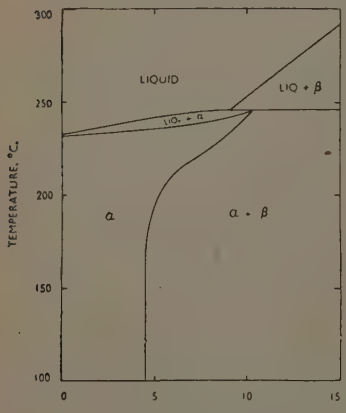


FIG. 2.—Tin-Rich End of Antimony–Tin Constitutional Diagram (Hanson and Pell-Walpole).

A number of alloys were chemically analysed, and since the results (Table I) were all close to the intended compositions, the remainder were assumed to be satisfactory.

Inverse-rate cooling curves were taken from approximately 50° C. above the liquidus on 200-g. samples at approximately 2° C./min., with continuous mechanical stirring to prevent segregation. The thermocouple was previously calibrated under the same conditions, and was used in conjunction

TABLE I.—*Results of Chemical Analysis.*

Intended Composition.		Analysis.	
Cu, %.	Sb, %.	Cu, %.	Sb, %.
10	0	10·06	...
0	50	...	50·35
0·5	2	0·48	1·95
0·5	10	0·51	10·00
0·75	10	0·76	10·02
0·75	0	0·75	...
1·0	2	1·00	2·03
1·0	8	1·02	8·10
1·25	2	1·27	2·05
1·25	10	1·24	10·11
2·0	6	1·97	5·90
3·0	2	2·92	2·05
3·0	14	3·00	13·82

with a potentiometer and chronograph, the plots being made at intervals of rather less than 1° C. Heating curves were plotted from 150° C. to temperatures just above the solidus, at a rate of 3° C./min., using specimens ½ in. dia. × 1 in. long, and drilled for the insertion of a bare thermocouple which was re-calibrated for use under these conditions. These specimens were prepared by chill casting, annealing for a month at 200°–210° C., and cooling slowly in the furnace. Arrest temperatures are given in Table II and are incorporated in the vertical sections (Figs. 10–22). The data on copper–tin alloys agree closely with the earlier work of Hanson, Sandford, and Stevens and have been incorporated in Fig. 3.

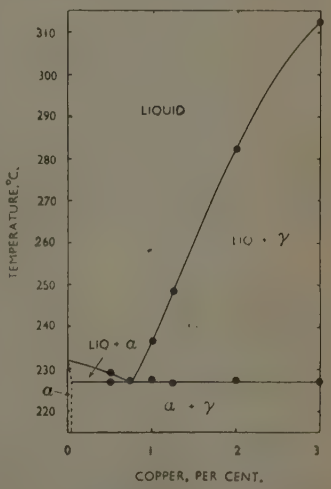
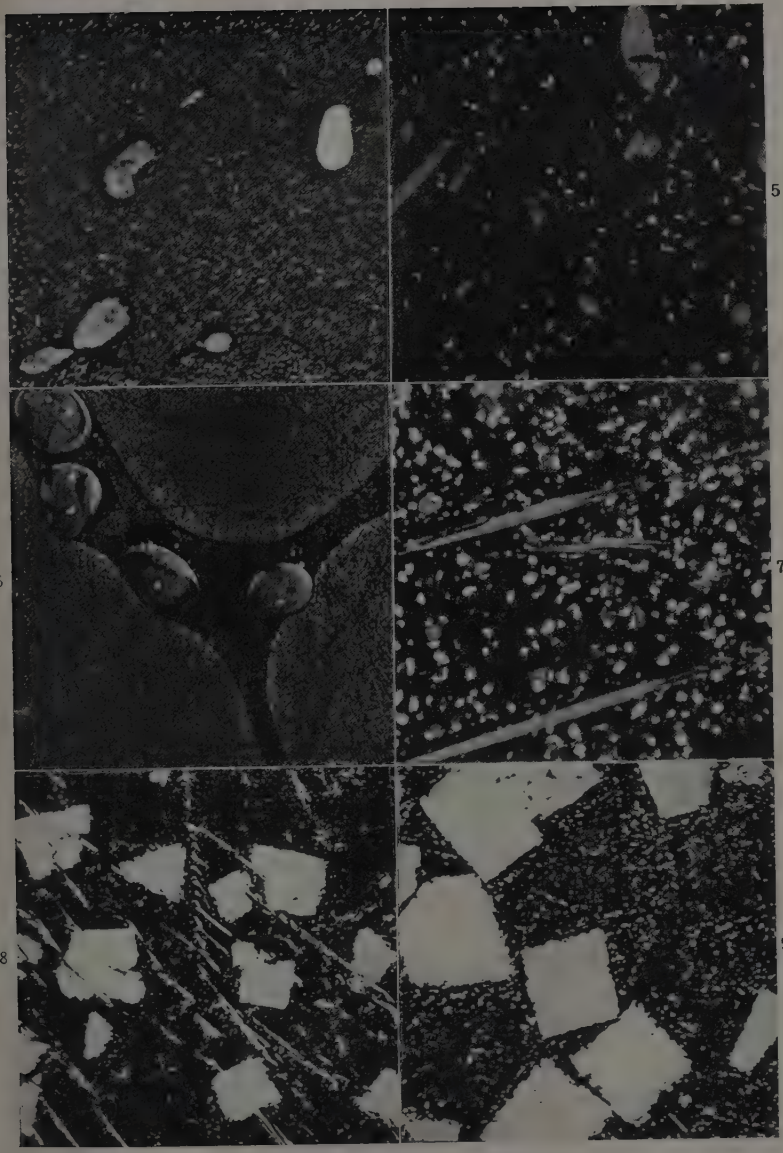


FIG. 3.—Tin-Rich End of Copper–Tin Constitutional Diagram.

All the alloys were examined metallographically in the cast state, to assist interpretation of the thermal data. For determining the phase boundaries in the solid state at different temperatures, chill-cast specimens were annealed for a month at 200°–210° C., cooled to room temperature in three days, reheated for 48 hr. at the temperature concerned, and water quenched.

TABLE II.—*Results of Thermal Analysis.*

Composition.		Arrest Temperatures, °C.					
		Cooling curves.			Heating curves.		
Cu, %.	Sb, %.						
0·5	2	233			229·5		
	4	237	231		231·5		
	6	240·5	234·5		233·5		
	8	244	243	237	236		
	10	260	243		239·5		
	12	271	242·5		239·5		
	14	285	242		239·5		
0·75	2	231·5	229·3				
	4	235	231				
	6	238	233·5				
	8	243					
	10	260	241				
1·0	2	233·5			229·5		
	4	235			231		
	6	238			233·5		
	8	241	239		236		
	10	256·5	243		239·5		
	12	270·5	245	240	239·5		
	14	283	247	241	239·5		
1·25	2	242·5	230·5				
	4	246	234	231			
	6	249	237				
	8	250·5	242	236			
	10	253	239·5				
	12	270	255	240			
	14	281	256	239·5			
2·0	2	282	231		229		
	4	282			231		
	6	282	238		233·5		
	8	282	244	241	237	239·5	
	10	282	256·5	241		239·5	
	12	282	268·5	239·5		239·5	
	14	282	277			239·5	
3·0	2	313	230·5		229		
	4	312·5	234	231·2	231·5		
	6	313	237·5		234		
	8	313	245·5	240	237·5	239·5	
3·0	10	313·5	257·5	239·5		239·5	
3·0	12	313	270	240		239·5	
3·0	14	313	279·5	239·5		239·5	
0·5	0	229	227				
0·75	0		227				
1·0	0	236·5	227·5				
1·25	0	248	226·5				
2·0	0	282	227·25				
3·0	0	313	227				



FIGS. 4–9.

For Captions, see Back of Plate.

[*To face p.* 118.

FIG. 4.—Copper ½, Antimony 10%. Quenched at 239° C. β (white) and γ (grey) in α (dark). × 400.

FIG. 5.—Copper 3, Antimony 3%. Annealed and slowly cooled to 20° C. β (white) and γ (grey) in α (dark). × 400.

FIG. 6.—Copper 3, Antimony 8%. Quenched from 239° C. γ globules and quenched liquid in α (dark), with traces of β (white). × 500.

FIG. 7.—Copper 2, Antimony 6%. Primary γ needles (grey) in matrix of α (dark) + γ (grey), with white β precipitate. × 450.

FIG. 8.—Copper 3, Antimony 12%. Primary γ needles, secondary γ needles + β cuboids in dark (α + γ) matrix, with traces of precipitated β. × 250.

FIG. 9.—Copper ½, Antimony 14%. Primary β cuboids (white) in dark (α + γ) matrix, with white β precipitate. × 350.

No phases were found other than those in the corresponding portions of the binary systems (Figs. 2 and 3). It was necessary to develop a special etching reagent for distinguishing SbSn from Cu_6Sn_5, since these constituents did not appear in their familiar cuboidal and needle-like forms, respectively, after heat-treatment, but as fine precipitates and rounded particles. In these conditions the standard etching reagents fail to distinguish them. The procedure adopted was as follows. The specimen was first etched in the standard reagent (2% nitric acid in alcohol). This stained the α dark and left both compound phases unattacked. The specimen was then immersed in a 20% aqueous solution of sodium sulphide, and a few drops of concentrated HCl added. The SbSn was unaffected, but the Cu_6Sn_5 was coloured brown (see Figs. 4–7, Plate X). Other typical microstructures are shown in Figs. 8 and 9, Plate X (etched in 2% HNO_3 in alcohol), and results of metallographic examination are shown in vertical and horizontal sections (Figs. 10–22, 27–32).

III.—The Liquidus Surface.

The liquidus surface (Fig. 23) is divided into three areas representing the primary separation of α (*ABCD*), β (based on SbSn) (*BCEF*), and γ (based on Cu_6Sn_5) (*DCEGH*), intersecting at the ternary peritectic point *C*, which represents the composition of the liquid in the reaction $\beta + \text{liq.} \rightleftharpoons \alpha + \gamma$. Along the groove *BC*, the reaction $\beta + \text{liq.} \rightarrow \alpha$ derived from the tin–antimony system, occurs. The temperature of this reaction falls with increasing copper content to that of the ternary peritectic at point *C*. Along the valley *DC*, the binary complex $\alpha + \gamma$ originating in the copper–tin system, separates. The temperature of this transition is raised progressively with increasing antimony content from 227° to 239·5° C. The groove *CE* corresponds to the simultaneous separation of β and γ.

IV.—Surfaces of Secondary Separation.

The surfaces of secondary separation are shown in Fig. 24.

The reaction $\beta + \text{liq.} = \alpha$ derived from the tin–antimony system, commences at the surface *DFHJ*. The other surface bounding this reaction can best be seen in vertical sections Figs. 19 (*BH*), 10, and 11 (*BE*).

Surfaces *DJK*, *DKLM* correspond to the commencement of secondary separation of $(\beta + \gamma)$ and surfaces *CDMN*, *BCDE* to the secondary separation of $(\alpha + \gamma)$.

The final stage of solidification is shown in Figs. 25 and 26, being the ternary peritectic plane and the solidus respectively. The ternary

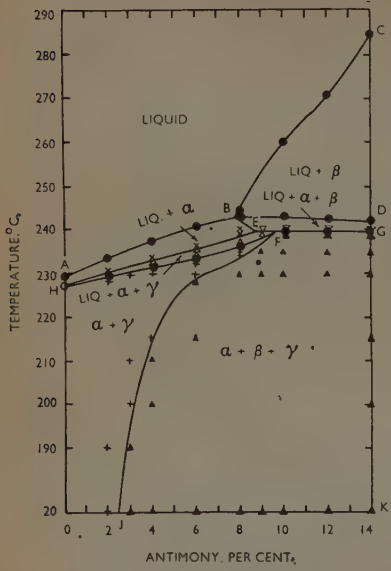


FIG. 10.—Section at 0·5% Copper.

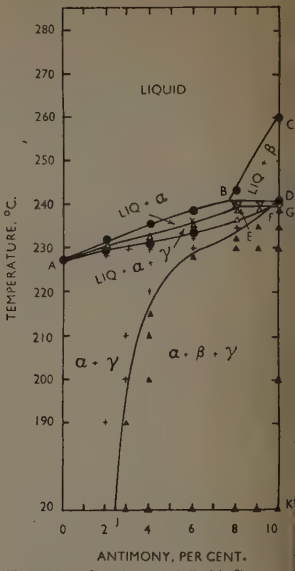


FIG. 11.—Section at 0·75% Copper.

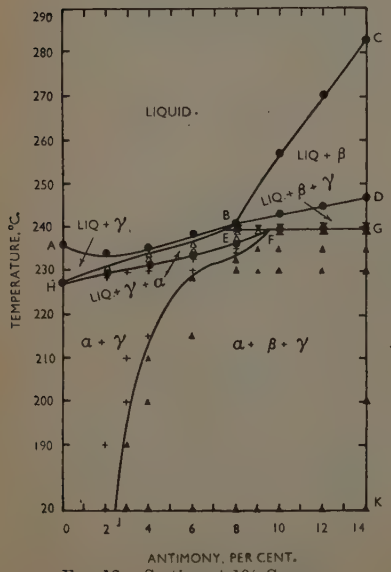


FIG. 12.—Section at 1% Copper.

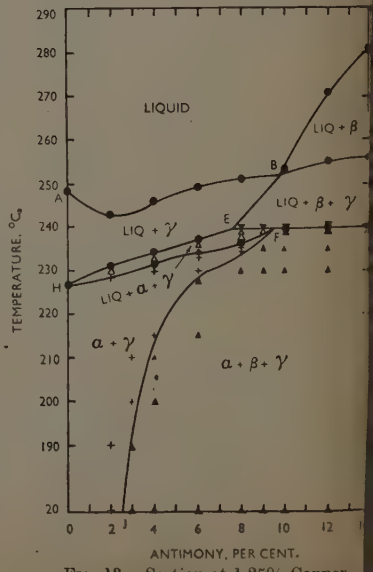


FIG. 13.—Section at 1·25% Copper.

KEY FOR VERTICAL AND HORIZONTAL SECTIONS:

Microscopical evidence.

- ● Thermal arrest.
- \+ $\alpha + \gamma$.
- × α + liquid.
- ▲ $\alpha + \beta + \gamma$.
- △ $\alpha + \gamma$ + liquid.
- ▽ $\alpha + \beta$ + liquid.
- ▼ $\beta + \gamma$ + liquid.

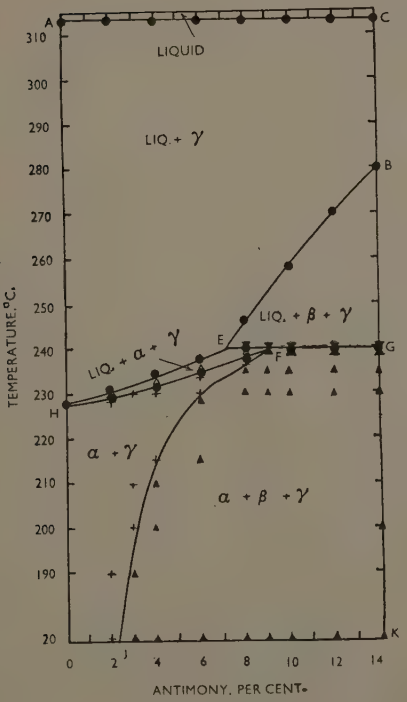


FIG. 14.—Section at 3% Copper.

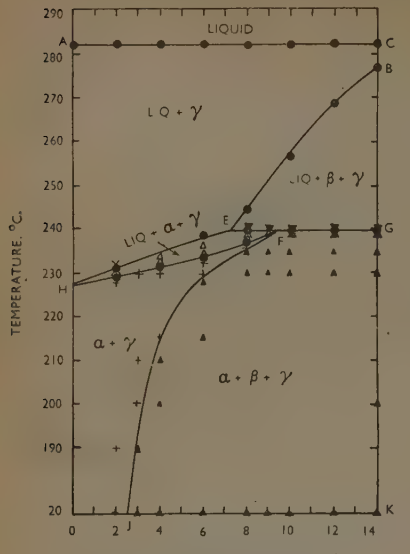


FIG. 15.—Section at 2% Copper.

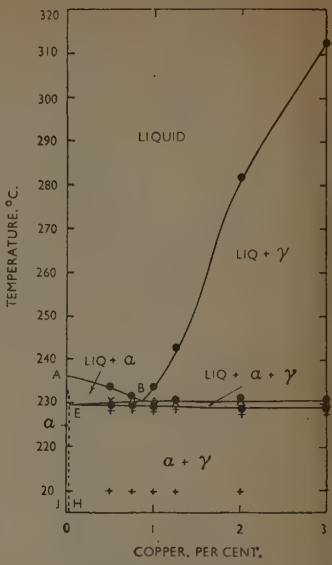


FIG. 16.—Section at 2% Antimony.

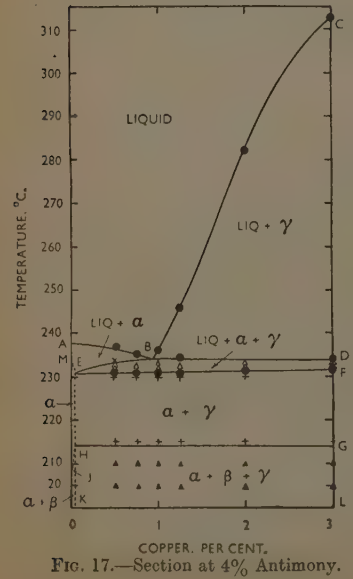


FIG. 17.—Section at 4% Antimony.

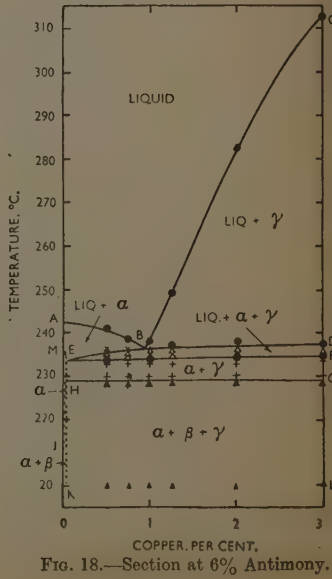


FIG. 18.—Section at 6% Antimony.

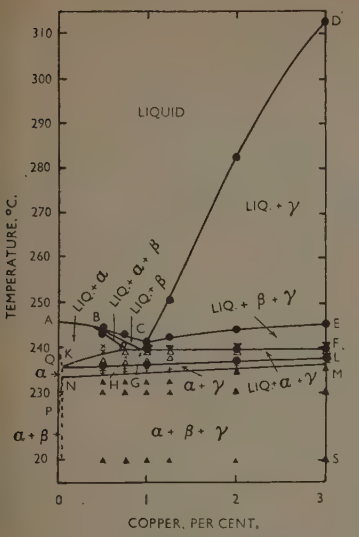


FIG. 19.—Section at 8% Antimony.

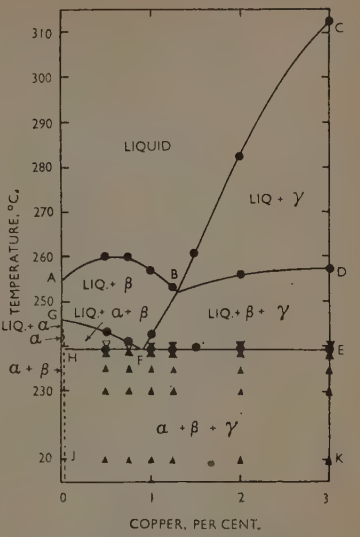


FIG. 20.—Section at 10% Antimony.

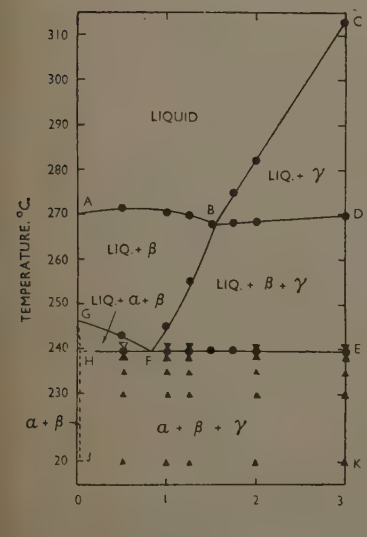


FIG. 21.—Section at 12% Antimony.

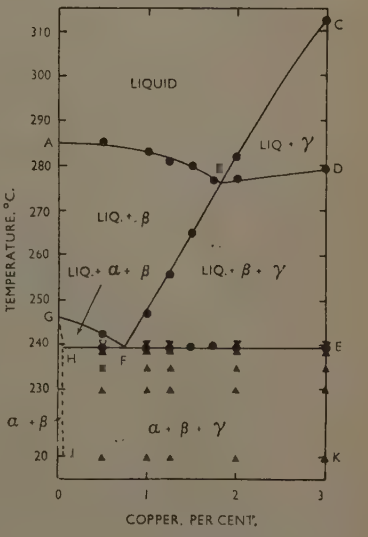


FIG. 22.—Section at 14% Antimony.

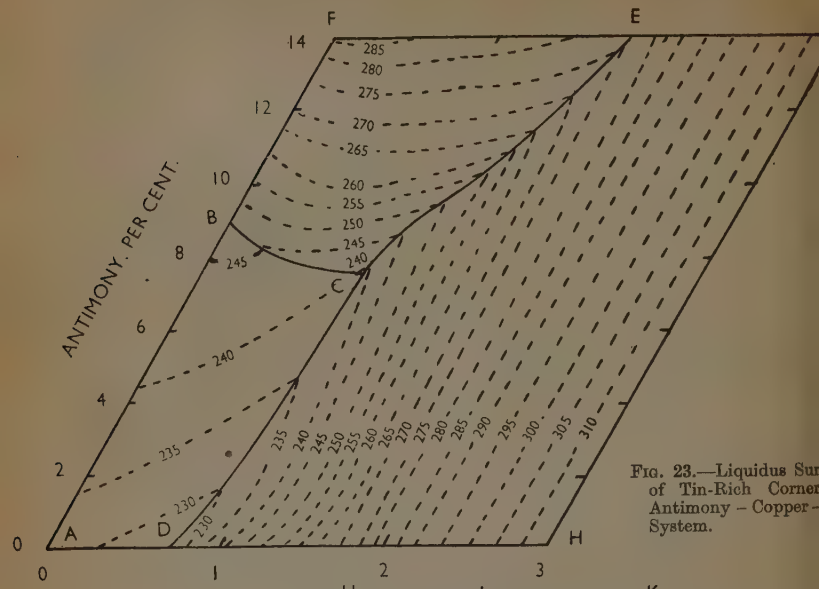


FIG. 23.—Liquidus Sur
of Tin-Rich Corner
Antimony – Copper –
System.

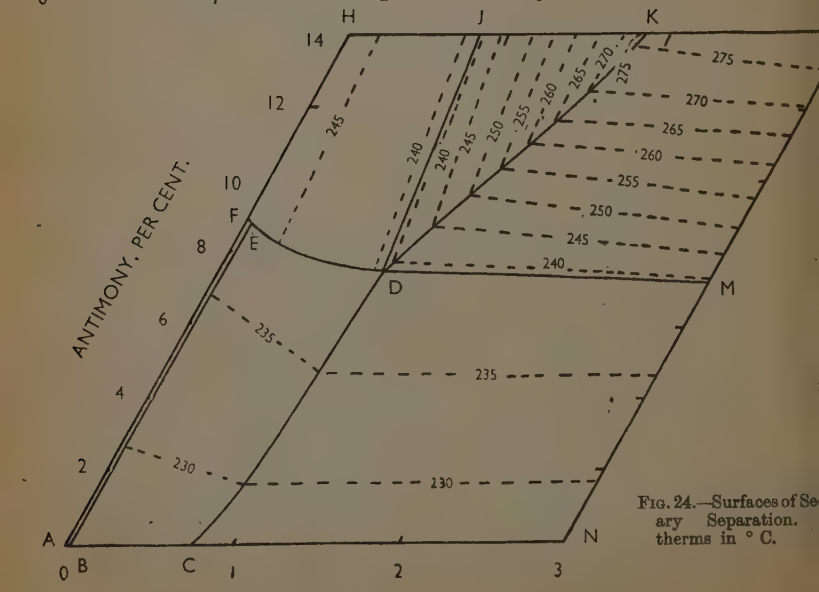


FIG. 24.—Surfaces of Se
ary Separation.
therms in ° C.

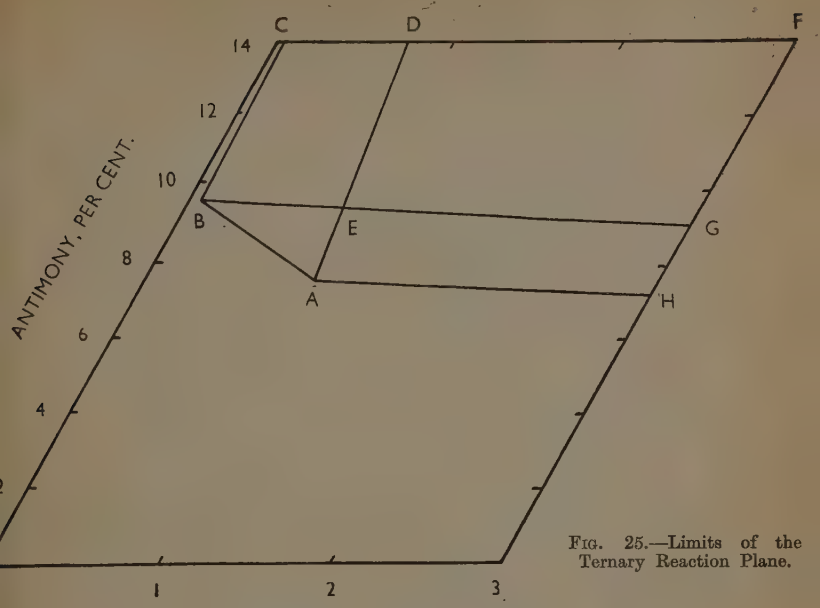


FIG. 25.—Limits of the Ternary Reaction Plane.

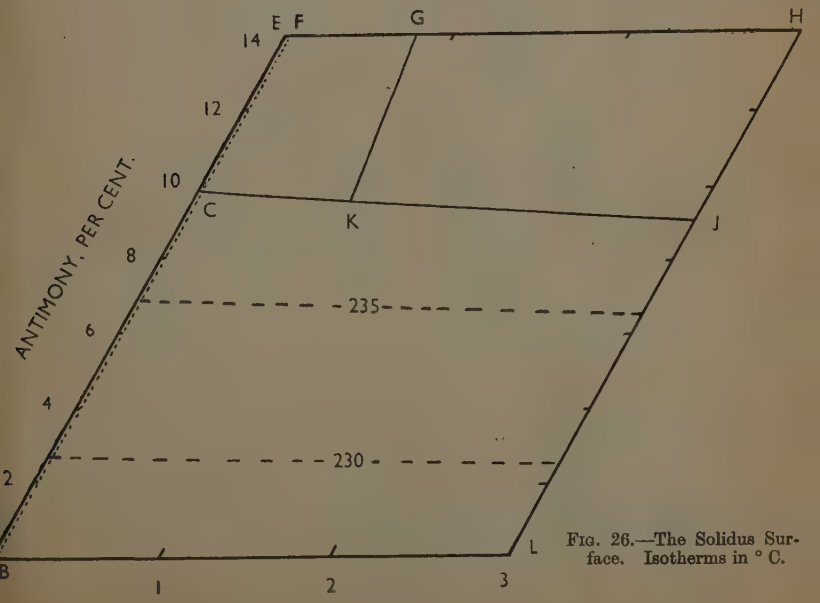


FIG. 26.—The Solidus Surface. Isotherms in ° C.

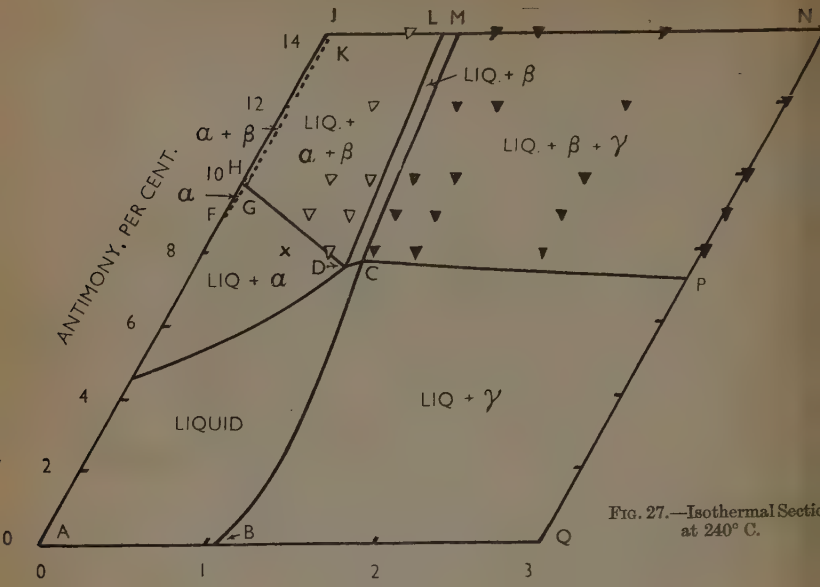


FIG. 27.—Isothermal Sectio at 240° C.

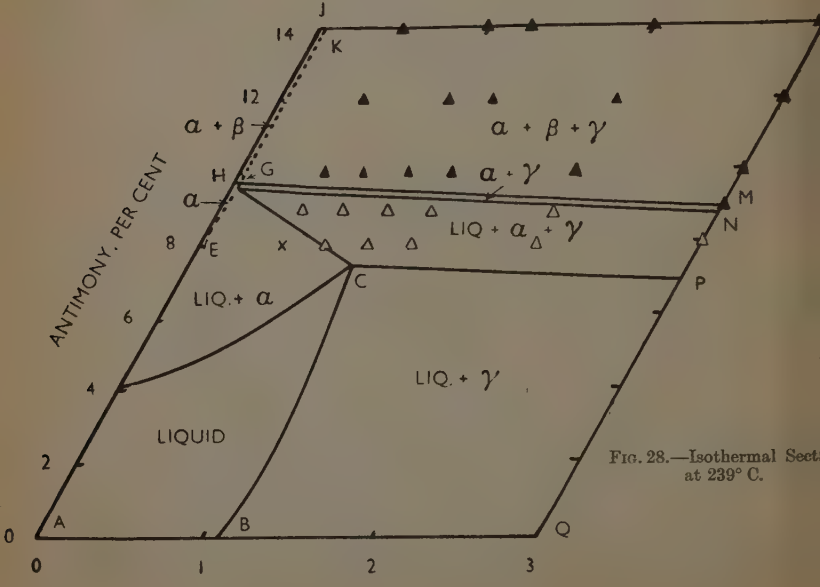


FIG. 28.—Isothermal Sect at 239° C.

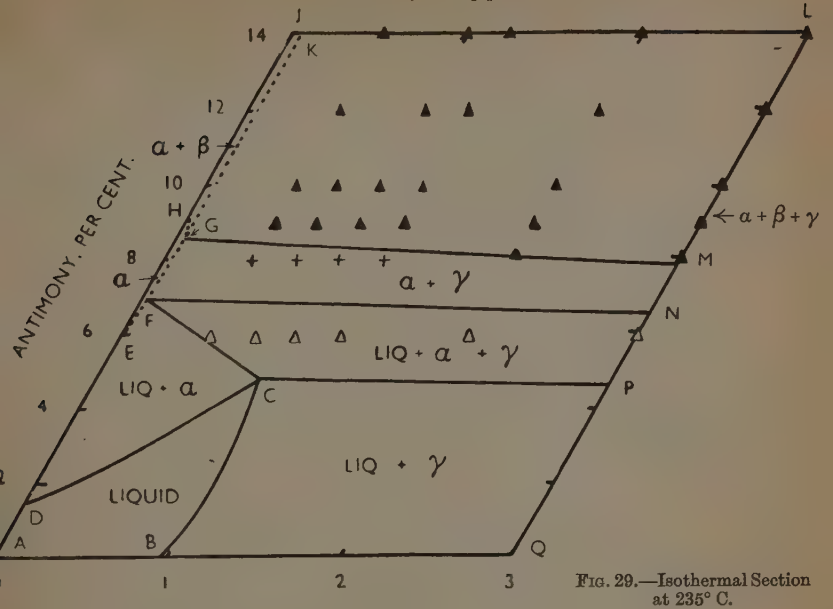


FIG. 29.—Isothermal Section at 235° C.

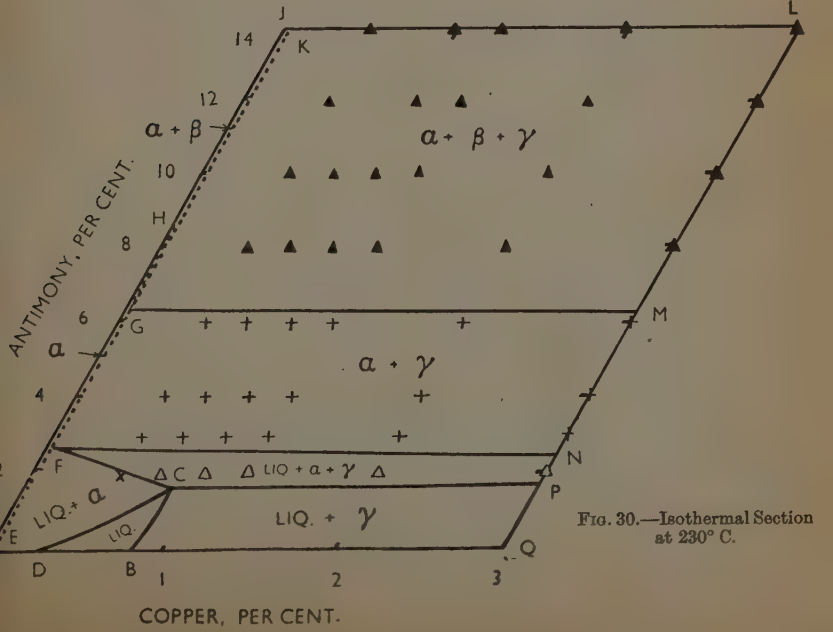


FIG. 30.—Isothermal Section at 230° C.

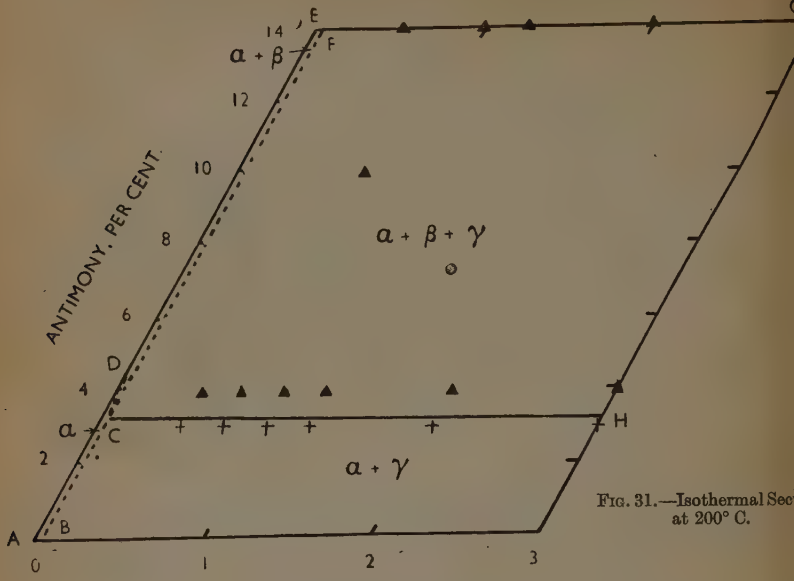


FIG. 31.—Isothermal Sec
at 200° C.

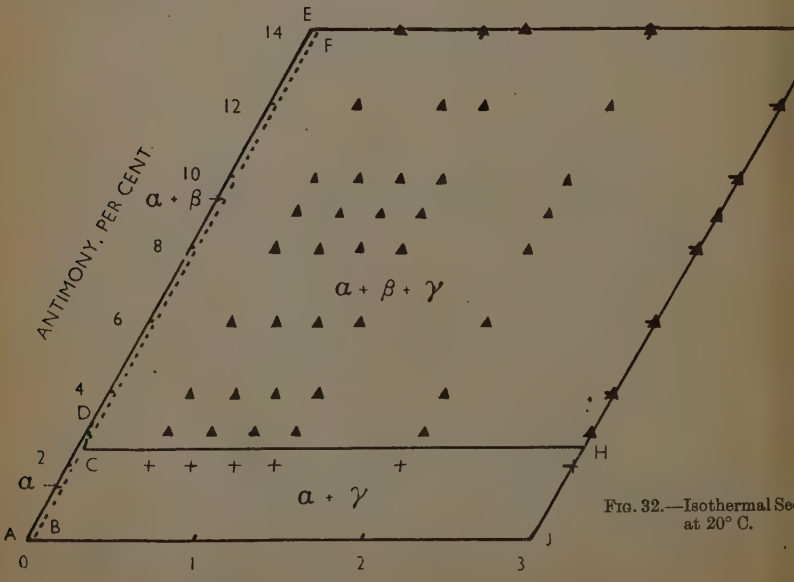


FIG. 32.—Isothermal Se
at 20° C.

peritectic reaction $\beta +$ liq. $\rightleftharpoons \alpha + \gamma$ occurs at 239·5° C., the composition of the liquid involved being antimony 7·6, copper 0·97%, tin remainder (point *A*). The α solid solution (point *B*) contains 9·8% antimony and probably less than 0·01% copper. The β and γ phases involved are likely to have compositions little different from the original binary phases SbSn and Cu_6Sn_5. This reaction takes place in a range of alloys considerably greater than has been covered by the present investigation. (The peritectic reaction is further illustrated in Figs. 27 and 28, showing horizontal sections of the space model immediately above and below the plane.)

Alloys whose compositions lie within the area *BCFG* of Fig. 25 complete their solidification by the ternary reaction, and this surface forms part of the solidus surface, as shown in Fig. 26 (area *CFHJ*). Alloys whose compositions lie within area *ABGH* of Fig. 25 consist of $\alpha + \gamma +$ liq. on cessation of the ternary reaction, and their solidus surface is part of *BCJL* of Fig. 26, which corresponds to the completion of solidification of the $\alpha + \gamma$ complex.

V.—The Constitution in the Solid State.

1. *Structures of Alloys in Equilibrium.*

Below the solidus, all alloys examined consist either of $(\alpha + \gamma)$ or of $(\alpha + \beta + \gamma)$. The solubility of antimony decreases with falling temperature rather more rapidly than in the corresponding binary tin–antimony alloys, and at room temperature it is appreciably lower in the ternary alloys. This effect can be seen by comparing the position of the $\alpha + \gamma/\alpha + \gamma + \beta$ boundary in Figs. 28–32. It is also shown clearly in the vertical sections at constant copper content (Figs. 10–15).

2. *Structures of Alloys in the As-Cast Condition.*

The structures of these alloys in the as-cast condition form several distinct groups, according to the various primary and secondary separations. Referring to Fig. 24, alloys within the area *ABEF* (for practical purposes coincident with binary antimony–tin alloys containing up to 9% antimony) consist of cored α with occasional traces of precipitated β. Within the area *BCDE* they consist of cored α with binary complex $(\alpha + \gamma)$. Owing to the relatively small amount of γ at the eutectic composition, this complex rarely shows the typical eutectic structure but consists of isolated particles of γ in a cored α matrix. Within the area *CDMN*, the alloys consist of primary needles, prisms, or star-like crystals of γ in the $(\alpha + \gamma)$ matrix (Fig. 7, Plate X), and in the area *DKLM*, of primary γ with secondary $(\beta + \gamma)$ in the

($\alpha + \gamma$) matrix (Fig. 8, Plate X). In the region *DFHJ*, the alloys consist of primary cuboid β in a matrix of ($\alpha + \gamma$) (Fig. 9, Plate X), and in the region *DJK*, of primary cuboid β with secondary ($\beta + \gamma$) in a matrix of ($\alpha + \gamma$).

In alloys of all groups, traces of precipitated β may occur in the cored α of the ($\alpha + \gamma$) complex, but the α is normally heavily supersaturated with respect to antimony, the effective metastable solubility of the latter in small chill castings such as lined bearings being of the order of 7%.

Most of the commercial tin-base bearing metals consist of alloys from the two groups in which the primary separation is γ. Alloys containing primary α are usually too soft, while those in which primary β separates show severe segregation of this constituent, owing to its low density as compared with the residual liquid. Secondary β of the ($\beta + \gamma$) complex does not segregate provided that a network of primary γ has formed first. This occurs in all alloys appreciably to the right of the ($\beta + \gamma$) valley.

Acknowledgements.

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THE CONSTITUTION OF ALUMINIUM–MANGANESE–MAGNESIUM AND ALUMINIUM–MANGANESE–SILVER ALLOYS, WITH SPECIAL REFERENCE TO TERNARY-COMPOUND FORMATION.*

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Synopsis.

In connection with the role of transitional metal solutes in aluminium-rich alloys, experimental studies of the systems aluminium–manganese–magnesium and aluminium–manganese–silver have been made. In the former system, equilibrium in solid aluminium-rich alloys involves the α, $MnAl_6$, and Mg_2Al_3 phases, and a ternary compound T(MnMg) which was previously unknown. The rate of attainment of equilibrium is low, and long annealing times are necessary. From the form of an isothermal diagram based on the results of 204 days' annealing at 400° C., the composition of T(MnMg) may be represented as $(Mn.Mg)_3Al_{10}$ or, nearly, $MnMg_2Al_{10}$. The examination of slowly cooled alloys suggests that T(MnMg) is formed peritectically from $MnAl_6$ and from $MnAl_4$, but the fields of primary separation have not been examined in detail.

Equilibrium in solid aluminium–manganese silver alloys involves, in the aluminium-rich region, only the α and $MnAl_6$ phases, and the γ phase of the aluminium–silver system. An isothermal established at 495° C. shows that the (α + $MnAl_6$) field is extensive, while no ternary compound exists in equilibrium with the α solid solution. In connection with this work, the solid solubility of silver in aluminium between 400° and 520° C. has been re-determined.

The results are discussed theoretically, and it is shown that T(MnMg) is analogous to the ternary E phase in the system aluminium–chromium–magnesium. Both occur at approximately the same electron : atom ratio of 2·37, assuming that transitional metal atoms absorb from the structures sufficient electrons to fill the vacancies in their atomic orbitals. The influence of atomic size relationships on the formation of ternary compounds is also briefly discussed.

I.—Introduction.

In the alloy systems aluminium–manganese–copper, aluminium–manganese–nickel, and aluminium–manganese–zinc, ternary compounds are found to enter into equilibrium with the primary aluminium-rich solid solution. It has been shown in previous communications [1, 2, 3] that these ternary compounds may be considered as analogous. They are based in each case on a ratio of aluminium to solute atoms of 4 : 1, and

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have an electron : atom ratio of 1·85, if it be accepted that, in aluminium-rich alloys, transitional metals absorb sufficient electrons per atom to fill the vacancies in their atomic orbitals. According to the theory of the electronic structures of the transitional metals of the first long period of the Periodic Table proposed by Pauling,[4] each of the metals chromium, manganese, iron, cobalt, and nickel has 5·78 electrons per atom in bonding orbitals; the remaining electrons derived from the 3*d* and 4*s* electron levels of the free atom are accommodated in atomic orbitals, which can contain a maximum of 4·88 electrons per atom. Thus, the metals from chromium to nickel possess, in atomic orbitals, respectively 0·22, 1·22, 2·22, 3·22, and 4·22 electrons per atom. The electrons in atomic orbitals maintain their spins parallel until 2·44 electrons per atom are present; above this number of electrons per atom, pairing of spins occurs, and the saturation magnetic moments at absolute zero of this series of metals are due to the number of electrons per atom which remain unpaired. Application of this theory indicates that chromium, manganese, iron, cobalt, and nickel have respectively 4·66, 3·66, 2·66, 1·71, and 0·61 vacancies per atom in their atomic orbitals. The results of a number of examinations of ternary aluminium-rich alloys suggest that, in this class of alloy, the vacancies in the atomic orbitals of the transitional metal are filled by electrons absorbed from the structure as a whole.[3, 5, 6, 7] The electron : atom ratio for an aluminium-rich aluminium–manganese–zinc alloy, for example, is calculated according to the assumption that, whereas aluminium and zinc contribute respectively three and two electrons per atom to the structure, manganese absorbs from the structure 3·66 electrons per atom.

The ternary compounds formed in alloys of aluminium and manganese with copper, nickel, and zinc are based upon the simultaneous satisfaction of an electronic condition, and a condition involving a ratio of 4 aluminium atoms to one solute atom. Whether or not the second condition can be satisfied in any given case will depend upon the atomic size relationships involved. In order to examine this aspect more closely, aluminium–manganese–cadmium alloys have been examined.[2] The substitution of cadmium for zinc leaves electronic conditions unaltered, so that on this account there would appear to be no reason why a ternary compound analogous to that found in the aluminium–manganese–zinc alloys should not occur. Since, however, the atom of cadmium is relatively much larger than that of zinc, the second condition, dependent on atomic sizes, is not satisfied, and no ternary compound enters into equilibrium with the aluminium-rich solid solution.

The present paper describes work on the systems aluminium–

manganese–magnesium and aluminium–manganese–silver, undertaken in order to study further the effect of alterations of size relationships on the occurrence of the ternary compounds of electron : atom ratio 1·85. The atomic diameter of silver (2·883 Å) is larger than that of copper (2·551 Å), while, judging from the solid solubilities in aluminium of zinc, magnesium, and cadmium, the effective size factor of magnesium is intermediate between those for zinc and cadmium.

II.—The System Aluminium–Manganese–Magnesium.

1. *Previous Work.*

The constitution of the binary aluminium–manganese alloys has been described in several recent papers, and is satisfactorily established. For convenience in reference, the aluminium-rich portion is reproduced here as Fig. 1, which embodies the results of Dix, Fink, and Willey,[8] Phillips,[9] and Butchers and Hume-Rothery.[10] The solid solubility of manganese in aluminium reaches a maximum of 1·32% at the eutectic temperature, 658·5° C. The eutectic composition is 1·95% manganese. At 710° C. and 4% manganese, $MnAl_6$ is formed peritectically from the liquid and $MnAl_4$.

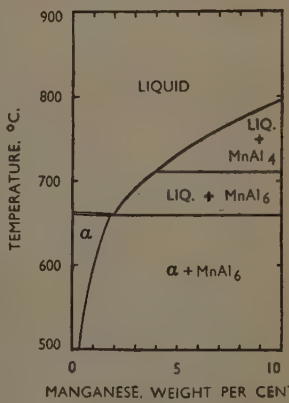

Fig. 1.

The binary equilibrium diagram for the aluminium–magnesium alloys is also satisfactorily established, and the aluminium-rich portion is shown in Fig. 2, which is taken from the diagram proposed by Raynor [11] from a consideration of the results of a large number of investigations. The solid solubility of magnesium in aluminium extends from 1·9% magnesium at 100° C. to 15·35% magnesium at the eutectic temperature, 450° C. The intermetallic phase β has a narrow range of homogeneity, and is based on the composition Mg_2Al_3. The γ phase has an appreciable range of homogeneity, and is based on the composition $Mg_{17}Al_{12}$. The crystal structures of the β and γ phases are complex.

The constitution of the ternary aluminium–manganese–magnesium system has been examined, in the range 0–2% manganese and 0–5% magnesium, by Little, Raynor, and Hume-Rothery,[12] Butchers and Hume-Rothery,[13] and Butchers, Raynor, and Hume-Rothery.[14] Within

this limited range of compositions, liquidus and solidus surfaces were established, and a solid-solubility isothermal at 500° C. was determined. No intermediate phases other than $MnAl_6$ were encountered in this work. It was also shown, by the analysis of $MnAl_6$ crystals extracted from a number of slowly cooled alloys, that the solubility of magnesium in $MnAl_6$ was very small, and was certainly less than 0·08% of magnesium under the conditions of the experiments.

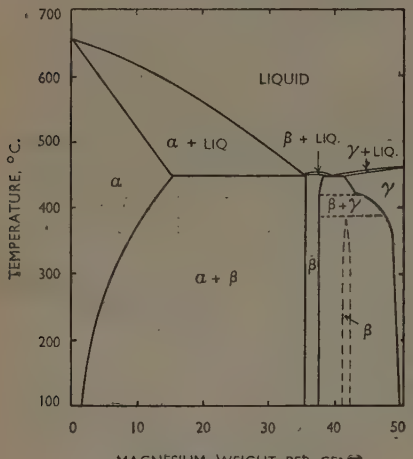

FIG. 2.

A more extensive investigation was made by Leemann,[15] who used alloys containing 0–12% manganese and 0–35% magnesium. The results obtained are summarized in Figs. 3 and 4, which represent respectively the surfaces of primary separation, and the constitution in the solid state at the end of solidification. No ternary phase was recognized in this work, and, according to Figs. 3 and 4, the equilibria for the aluminium-rich alloys in the solid state involve only the primary solid solution (α), $MnAl_6$, and Mg_2Al_3. At higher alloy contents, Mg_2Al_3 can enter into equilibrium with both $MnAl_6$ and $MnAl_4$. The eutectic temperature (437° C.) and the eutectic valley (E_1 to E_T in Fig. 3) were determined by thermal analysis. The other boundaries, and the phase fields in Fig. 4, were based mainly on the micrographic analysis of alloys in the "as-cast" condition. Since Leemann's results would not be expected to represent equilibrium conditions, it was decided to re-examine the constitution of these alloys in the solid state.

2. *Experimental Methods.*

(a) *Materials.*

For the preparation of the alloys, super-purity aluminium, obtained from the British Aluminium Company, Ltd., and pure magnesium (99·97%), obtained from Messrs. F. A. Hughes and Co., Ltd., were used, together with aluminium–manganese master alloys. Two master alloys

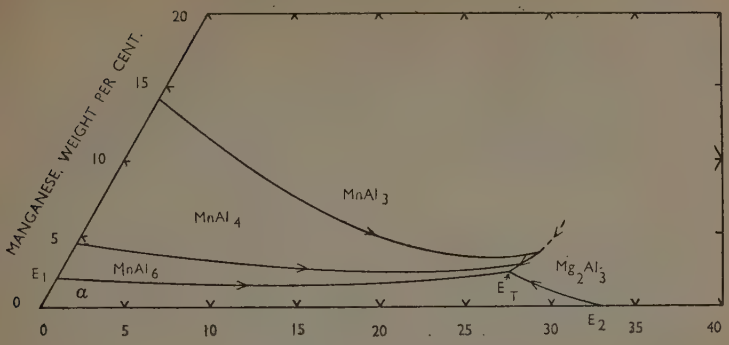
MANGANESE. WEIGHT PER CENT.
20
15
10
5
0
MnAl3
MnAl4
MnAl6
E1
α
Mg2Al3
ET
E2
0
5
10
15
20
25
30
35
40
MAGNESIUM. WEIGHT PER CENT.

FIG. 3.

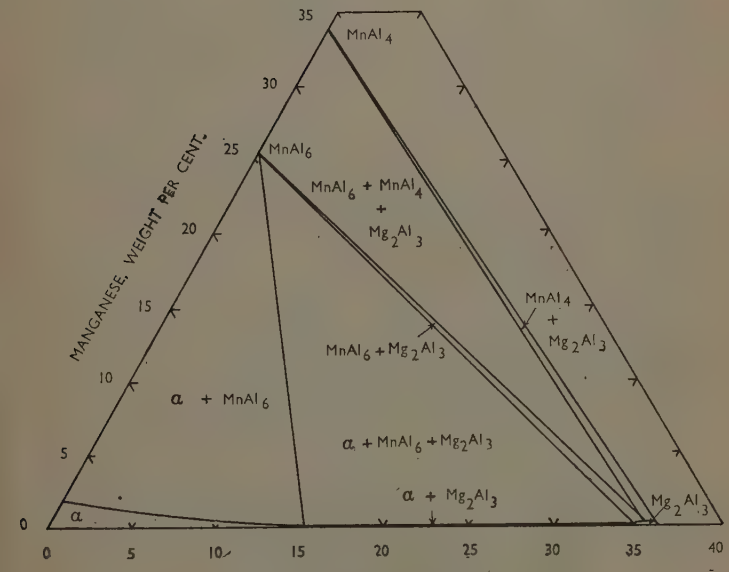
MANGANESE. WEIGHT PER CENT.
35
30
25
20
15
10
5
0
MnAl4
MnAl6
MnAl6 + MnAl4 + Mg2Al3
MnAl4 + Mg2Al3
MnAl6 + Mg2Al3
α + MnAl6
α + MnAl6 + Mg2Al3
α + Mg2Al3
α
Mg2Al3
0
5
10
15
20
25
30
35
40
MAGNESIUM. WEIGHT PER CENT.

FIG. 4.

were used, containing respectively 9·52 and 5·25% manganese; both alloys were prepared from pure materials.

(b) *Casting and Annealing.*

Since previous experience had shown that, for the attainment of equilibrium in a reasonable time in systems of this type, a very fine chill-cast microstructure was necessary, alloys, prepared by melting the appropriate quantities of metal in an alumina-lined crucible, were cast into the ice-cooled mould described by Wakeman and Raynor.[2] Sections of the resulting ingots were inserted into alumina sheaths, and sealed up in evacuated hard-glass tubes. The tubes were placed in holes bored in an aluminium cylinder (Fig. 5), which was placed in an automatically controlled resistance furnace. By this means, small temperature gradients and fluctuations inside the furnace were minimized. Annealing treatments were terminated by quenching the alloys individually in cold water.

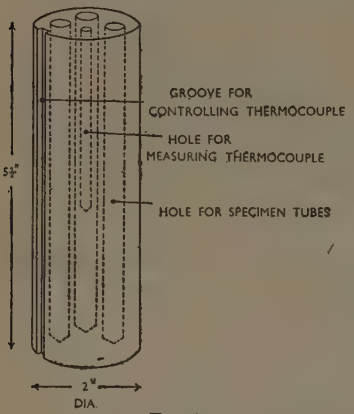

FIG. 5.

(c) *Polishing and Etching.*

Specimens of annealed alloys for micrographic examination were prepared in the usual manner, and polished with "Silvo" on Selvyt cloth, followed by levigated alumina applied on the same material. No difficulty was encountered, except in the case of alloys relatively rich in magnesium. These alloys were brittle, and required very light pressure during the initial stages on emery papers.

During the course of the work, the β and γ phases of the system aluminium–magnesium were recognized, together with $MnAl_6$ and $MnAl_4$. In addition, a further micrographic constituent was observed. This was lighter in colour, and in lower relief, than $MnAl_6$, and was identified as a ternary compound. Etching for periods of 10 sec. in a 20% aqueous nitric acid solution at 70° C. blackened Mg_2Al_3, and left the intermediate phases of higher manganese content relatively unaffected. Distinction between the latter constituents was given by an

aqueous etching solution containing 2% of sodium hydroxide and 5% of sodium carbonate. Etching for 30 sec. in this reagent stained $MnAl_6$ blue, and $MnAl_4$ brown. The ternary-compound phase was only slightly stained, and appeared a light grey. Mg_2Al_3 was unaffected by the alkaline reagent, while the aluminium-rich solid solution was slightly darkened.

(d) *Analytical Control.*

The actual micrographically-examined specimens of all critical annealed solid alloys were analysed for manganese and magnesium, after the circumferential layers had been filed away to remove any portions of the specimen from which magnesium might have been lost by evaporation during annealing. The analyses were performed by Messrs. A. J. Hawkes and P. Wingrove, to whom the authors are indebted for their careful work.

(e) *Nomenclature.*

For convenience in description, individual alloys are referred to in terms of their composition. Thus, the term " alloy 2·5/7·5 " refers to an alloy containing 2·5% manganese and 7·5% magnesium.

3. *The Constitution in the Solid State.*

For preliminary work, a series of 17 alloys containing a maximum of 3·5% manganese and 5–36% magnesium was prepared. Sections of the chill-cast ingots were annealed for 28 days at 400° C., which was the highest convenient temperature below that of the ternary eutectic. The microstructures of the annealed alloys were somewhat difficult to interpret, particularly at the higher magnesium contents, and it was clear that equilibrium had not been attained. All specimens were, therefore, re-annealed for a further 36 days, giving a total annealing period of 64 days. After this treatment, alloy 3·5/5·00 contained the α and $MnAl_6$ phases, while alloy 3·5/10·00 showed particles, in addition to those having the etching characteristics of $MnAl_6$, which appeared pale grey. The etching characteristics of the latter phase were unlike those of any of the binary aluminium–manganese or aluminium–magnesium phases which could enter into equilibrium with the primary solid solution at this composition; this phase was therefore identified as a ternary phase *T*(MnMg). Alloys with higher percentages of magnesium showed the same three phases; the amount of Mg_2Al_3 increased, while the amount of α decreased, until, at the composition 3·0/30·0, the alloy consisted almost entirely of the Mg_2Al_3 and *T*(MnMg) phases. In addition to the α, *T*(MnMg), and Mg_2Al_3 phases, alloys containing 25–29% magnesium,

showed increasing amounts of $MnAl_4$; the presence of four phases showed that equilibrium had not been attained. Alloys with 33–36% magnesium contained, in addition to Mg_2Al_3, T(MnMg), and $MnAl_4$, the γ phase of the aluminium–magnesium system, while alloys 3·0/30·0, 3·0/31·0, and 3·0/32·0, which consisted mainly of the Mg_2Al_3 and T(MnMg) phases, also contained small amounts of $MnAl_4$. Even after 64 days of annealing, therefore, many of the alloys were not in equilibrium, but the

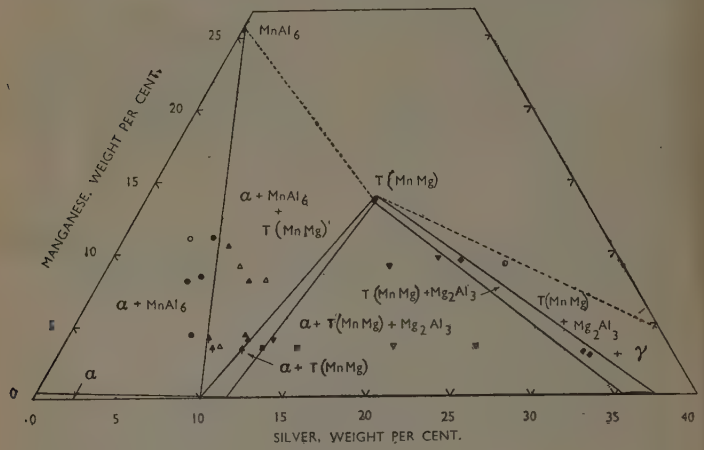

FIG. 6.

○ ● $\alpha + MnAl_6$.
△ ▲ $\alpha + MnAl_6 + T$(MnMg).
■ $\alpha + T$(MnMg).
▽ ▼ $\alpha + T$(MnMg) + Mg_2Al_3.
◆ T(MnMg) + Mg_2Al_3.
◐ T(MnMg) + $Mg_2Al_3 + \gamma$.
Traces of third phase.

results showed clearly that the constitution in the solid state was more complex than that reported by Leemann.

In order to define the phase boundaries, and to obtain an estimate of the composition of T(MnMg), 27 further alloys were prepared, and annealed for 204 days at 400° C. in an attempt to obtain equilibrium. The results of the subsequent micrographic examination are shown in Fig. 6, in which analysed alloys are distinguished by black symbols.

In spite of the very long annealing treatment, certain alloys contained very small amounts of an extra phase. Thus, some of the larger T(MnMg) crystals present in alloy 3·93/12·60 contained small inclusions

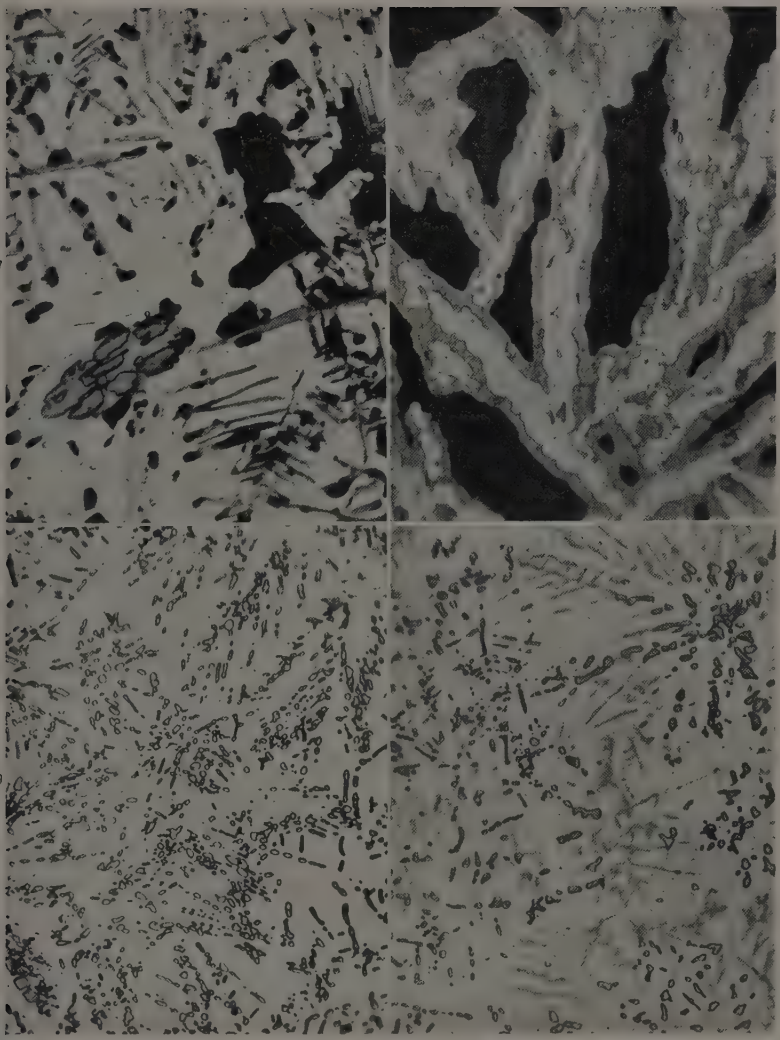

FIG. 7.—Alloy 3·93/12·60 Annealed 400° C. $\alpha + T(MnMg) + Mg_2Al_3$; inclusions of $MnAl_6$ in $T(MnMg)$.

FIG. 8.—Alloy 9·01/23·90 Annealed 400° C. $T(MnMg) + Mg_2Al_3 + \gamma$.

FIG. 9.—Alloy 4·3/7·3 Annealed 400° C. $\alpha + MnAl_6$.

FIG. 10.—Alloy 3·5/9·5 Annealed 400° C. $\alpha + MnAl_6 + T(MnMg)$.

× 500.

[*To face p.* 138.

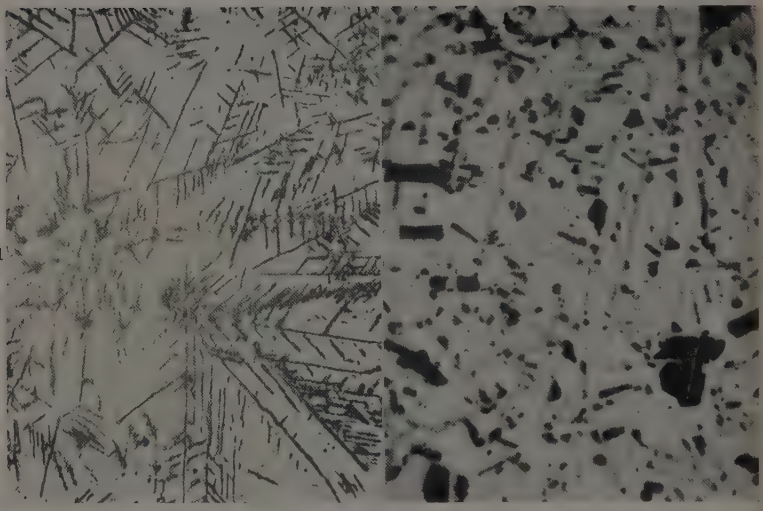

FIG. 11.—Alloy 4·11/10·95 Annealed 400° C. $\alpha + T(MnMg)$.
FIG. 12.—Alloy 3·32/14·26 Annealed 400° C. $\alpha + Mg_2Al_3 + T(MnMg)$.
× 500.

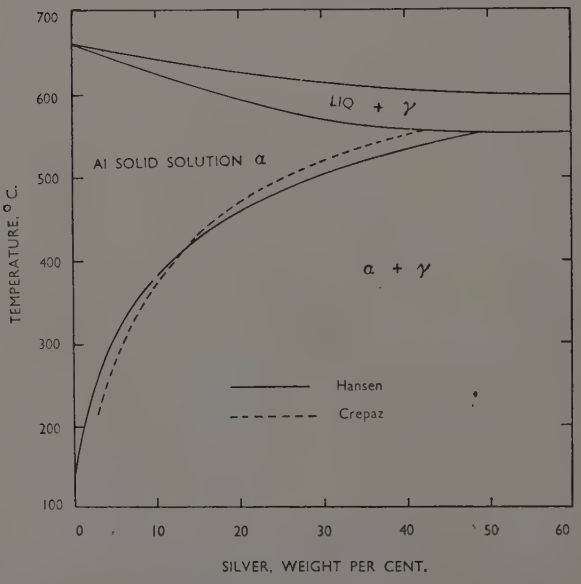

FIG. 13.

of $MnAl_6$. Fig. 7 (Plate XI) shows an area of this alloy after successive etching treatments in the alkaline and nitric acid reagents. The *T*(MnMg) particles are a pale grey, while Mg_2Al_3 is stained heavily; one of the *T*(MnMg) particles contains inclusions of $MnAl_6$. In equilibrium, this alloy would certainly consist of the α, *T*(MnMg), and Mg_2Al_3 phases, though the complete removal of the very small $MnAl_6$ inclusions would require a prohibitively long annealing treatment. Similar very small $MnAl_6$ inclusions were detected in alloys 9·07/17·1, 9·53/21·03, 9·80/19·62, and 9·01/23·90, but have been neglected in drawing Fig. 6. The microstructure of alloy 9·01/23·90 (Fig. 8, Plate XI) showed the *T*(MnMg) and Mg_2Al_3 phases, and a phase which was stained a light brown in the nitric acid reagent. This phase was identified as the γ phase of the aluminium–magnesium system.

Further typical microstructures are given in Figs. 9, 10, and 11 (Plates XI and XII), for which the alkaline reagent was used, while Fig. 12 (Plate XII) shows a characteristic microstructure, using the nitric acid reagent.

Fig. 6 shows that a ternary compound *T*(MnMg) enters into equilibrium with the primary solid solution in the system aluminium–manganese–magnesium. The position of the *T*(MnMg) phase shown is based on the structures of the annealed alloys, and on consideration of the relative amounts of the various phases present in these alloys. Its composition cannot differ greatly from manganese 13·5, magnesium 13·7, and aluminium 72·8%, and is more fully discussed below.

4. *Slowly Cooled Alloys.*

In order to confirm the presence of *T*(MnMg) at higher temperatures, and to obtain, if possible, suitable samples of the compound for analysis, an investigation was made of the structure of alloys slowly cooled at 1·5° C./min. from the liquid state. Ten alloys containing 2–4% manganese and 10–28% magnesium were prepared, and the ingots obtained after slow cooling were sectioned longitudinally and examined microscopically.

The phases present after slow cooling were the same as those encountered in the annealing work, and the presence of *T*(MnMg) was clearly established. The microstructures were, however, complex and difficult to interpret. All specimens contained the aluminium-rich solid solution and Mg_2Al_3. In addition, certain specimens contained needles of hexagonal cross-section, which were identified as $MnAl_4$, generally surrounded by thick sheaths of *T*(MnMg). In other alloys, $MnAl_6$ crystals were observed to be surrounded by thick sheaths of the ternary compound; in some cases, the $MnAl_6$ crystals themselves contained cores of $MnAl_4$.

From this work, T(MnMg) appears to be formed peritectically from $MnAl_4$ and also from $MnAl_6$. No alloy was obtained in which T(MnMg) crystals were observed free from cores of other material, and these results suggested that the primary T(MnMg) field was confined to a very small range of compositions near to the composition of the ternary eutectic. For this reason, and because no samples containing uncored T(MnMg) crystals were obtained, it proved impossible to prepare, by electrolytic extraction, a pure sample of the ternary compound for analysis.

At this stage of the work, information was received that an investigation of the constitution of aluminium–manganese–magnesium alloys above the solidus was in progress at the Research Laboratories of the British Aluminium Company, Ltd., and that very similar results were being obtained. In order to avoid duplication of work, the present experiments on the constitution of the alloys above the solidus were discontinued, since it had already been shown that no progress could be made towards the isolation of the compound T(MnMg) by electrolytic extraction from slowly cooled specimens.

5. *Further Experiments.*

Since no samples of T(MnMg) could be obtained by electrolytic extraction from slowly cooled alloys, attempts were made to extract the compound from alloys which had been annealed to equilibrium at 400° C. The alloys chosen were 4·11/10·96 ($\alpha + T$(MnMg)) and 2·93/32·1 ($Mg_2Al_3 + T$(MnMg)). The small-scale electrolytic-extraction apparatus described by Wakeman and Raynor [2] was used, and a number of acidic reagents were tried as electrolytes. No adequate residue of T(MnMg) was obtained in any experiment, owing to the reactivity towards the electrolyte of the compound crystals.

A partial separation of α and T(MnMg) was obtained by filing the annealed alloy 4·11/10·96, and grinding the filings in an agate mortar. The ductile particles of aluminium-rich matrix were flattened, but the more brittle compound particles were reduced to a fine powder. The whole was sieved through a 250-mesh gauze, and the finer portion, which was richer in T(MnMg) than the original filings, was used for X-ray experiments. An X-ray diffraction pattern, obtained using monochromatic iron K_α radiation, showed many faint lines in addition to the dense lines from the face-centred cubic aluminium-rich material. The pattern of extra lines did not resemble the diffraction patterns of any of the phases occurring in the binary aluminium–manganese and aluminium–magnesium systems, and confirmed the presence of a ternary phase.

6. *Summary.*

The experiments with slowly cooled alloys, and the more detailed annealing work in the solid state, show that, in the system aluminium–manganese–magnesium, a ternary compound *T*(MnMg) exists in equilibrium with the primary solid solution. This does not agree with the constitution as reported by Leemann, according to whom only $MnAl_6$ and Mg_2Al_3 enter into equilibrium with the aluminium-rich solid solution. The existence of the ternary phase has been confirmed, however, by X-ray experiments, and by work in progress at the Research Laboratories of the British Aluminium Company, Ltd.

The approximate composition of the ternary phase is 13·5% manganese and 13·7% magnesium, or, in atomic percentages, 7·0 at.-% manganese and 16·2 at.-% magnesium. The atomic composition is $(Mn.Mg)_3Al_{10}$, or almost $MnMg_2Al_{10}$. Although the compound may possess a range of homogeneity, the work on the constitution of aluminium–manganese–magnesium alloys in the solid state (Fig. 6) makes it very improbable that this range includes the composition $(Mn.Mg)Al_4$, while the electron : atom ratio of 2·37 is much too high for analogy with the ternary compounds which occur in the alloys of aluminium and manganese with copper, nickel, and zinc, respectively. The ternary compound *T*(MnMg) is therefore not to be regarded as a member of the series of compounds of electron : atom ratio 1·85, based on a ratio of four aluminium atoms to one solute atom.

III.—The System Aluminium–Manganese–Silver.

1. *Previous Work.*

The constitution of the aluminium–manganese alloys has already been considered. The general form of the equilibrium diagram for the aluminium-rich aluminium–silver alloys is well established, but the results reported by different workers [16, 17, 18, 19] differ in detail, particularly with regard to the solid-solubility limit of silver in aluminium. Fig. 13 (Plate XII) shows the aluminium-rich region of the equilibrium diagram, based on the results of Hansen,[17] with which the more recent work of Guertler [19] is in substantial agreement. The dotted curve represents the solid-solubility values reported by Crepaz.[18] Since Hansen used aluminium of purity 99·74% (silicon 0·1, iron 0·16%), and since the material used by Crepaz was even less pure (aluminium 99·3%), it was considered advisable to re-determine a portion of the primary solid solubility in the present work. The system is notable for the very extensive solubility of silver in solid aluminium, which extends up to 52% by weight at the eutectic temperature of 558° C.

No work on the ternary system aluminium–manganese–silver has been reported in the literature.

2. *Experimental Methods.*

(a) *Materials.*

The aluminium used was from the same sample as that described previously; assay silver, supplied by Messrs. Johnson, Matthey and Company, Ltd., was used in the preparation of the alloys. Two manganese-bearing master alloys were employed, one containing 5·12 and the other 12·95% manganese; the iron and silicon contents did not exceed respectively 0·002 and 0·001% for the dilute alloy, and 0·0175 and 0·0065% for the more concentrated alloy.

(b) *Casting and Annealing.*

Casting and annealing methods were closely similar to those described in Part II.

(c) *Polishing and Etching.*

The only modification introduced into the polishing technique was the omission of the final treatment with aqueous alumina suspensions, since these were found to cause pitting of the surface. The final polish was given by " Silvo " on Selvyt cloth.

Only three phases could be detected in the alloys examined. These were the aluminium-rich solid solution, $MnAl_6$, and the γ phase of the binary aluminium–silver system. These phases could be distinguished in the unetched condition; the $MnAl_6$ phase appeared light grey, while the γ phase was a pale yellow. Many etching reagents were examined in an attempt to improve the contrast between the γ phase and the aluminium-rich solid solution (α), but none could be regarded as entirely satisfactory. The most reliable were aqueous solutions of hydrofluoric acid, and the alkaline reagent described in Part II. Both caused somewhat irregular staining of the aluminium-rich matrix, particularly near grain boundaries. The nature and distribution of this effect, especially in specimens which were mounted for examination in plastic, suggest that it was caused by age-hardening of the water-quenched alloys. Barrett, Geisler, and Mehl [20] reproduce photomicrographs showing analogous effects in the report of their work on the age-hardening of aluminium–silver alloys.

(d) *Analytical Control.*

All critical alloys were analysed for silver and manganese, and are distinguished in the diagrams by black symbols.

3. *The Binary System Aluminium–Silver.*

Seven binary alloys containing 10–40 wt.-% silver were prepared, and annealed *in vacuo* at various temperatures for periods of three to ten days. In some cases, specimens were given successive annealing treatments at different, decreasing temperatures; between all such treatments the specimens were cold worked, by squeezing in a vice, to hasten diffusion on re-annealing. Annealing treatments were so

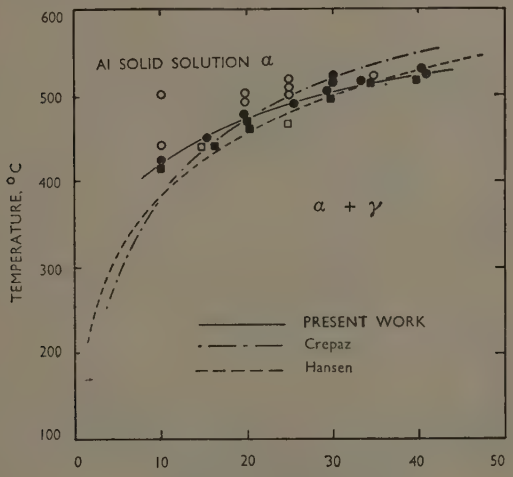

FIG. 14.

	Analysed.	Unanalysed.
Single-phase α alloys . . .	●	○
Two-phase α + γ alloys . . .	■	□

arranged that in all cases alloys which were duplex at equilibrium received a much longer treatment than those which were homogeneous at equilibrium, while in general the duplex specimens were produced by re-annealing alloys which had become homogeneous at a higher temperature.

The results of this work are shown in Fig. 14, in which the solubility curves due to Hansen and to Crepaz are given for comparison. According to the present experiments, the solid solubility of silver in aluminium is less at the lower temperatures, and greater at the higher temperatures, than previously reported. It is significant that Hansen's work bears a similar relationship to that of Crepaz, so that it is probable that the

solubility relationships are sensitive to purity of materials in this system. Progressive improvement in purity would appear to lead to higher maximum solid-solubility values. It is also to be noted that, at the highest temperature investigated, the solid-solubility curve becomes almost horizontal. For the purposes of the present paper, this point is unimportant; further experiments, however, are in progress to investigate the effect more fully.

4. *The Constitution in the Solid State.*

For preliminary experiments a series of alloys containing 5–3·6% manganese and 4–32% silver was prepared, and annealed *in vacuo* for 28 days at 495° C., this temperature having been shown to be below the melting point of the alloys richest in silver. Micrographic examination of the annealed and quenched specimens showed that, below 24% silver, only the α and $MnAl_6$ phases were present, except in the case of alloy 5·0/4·0, in which small amounts of the metastable aluminium–manganese *G* phase described by Little, Raynor, and Hume-Rothery,[21] were detected. Alloys containing more than 24% silver contained, in addition to the α and $MnAl_6$ phases, the γ phase of the aluminium–silver system. The results of this work showed, therefore, that no ternary compound exists in the aluminium–manganese–silver system, since equilibrium in the aluminium-rich alloys involves only the α, $MnAl_6$, and γ phases.

In order to define the boundaries of the phase fields more closely, 20 further alloys were prepared, and annealed for 120 days at 495° C. The long annealing treatment was given to ensure as far as possible the attainment of equilibrium and the absorption of any metastable *G* compound. In agreement with the preliminary work, only the three phases α, $MnAl_6$, and γ could be recognized in the annealed alloys, and the results are summarized in Fig. 15, in which the positions and structures of the preliminary series of alloys are also plotted. The limit of the α field on the binary aluminium–silver axis is taken from Fig. 14, while the extent of the solid solubility of silver in $MnAl_6$ has been drawn in accordance with experiments on the silver content of $MnAl_6$ crystals extracted from slowly cooled melts (see below). It will be appreciated that, since the aluminium-rich boundary of the $MnAl_6$ phase field is almost in line with the $(\alpha + MnAl_6)/(\alpha + MnAl_6 + \gamma)$ phase boundary, no independent evidence on the solubility of silver in $MnAl_6$ at 495° C. can be obtained from the experiments on the constitution in the solid state.

The system aluminium–manganese–silver therefore contains no ternary compound in equilibrium with the primary solid solution. There

is a very extensive ($\alpha + MnAl_6$) field, and the ($\alpha + MnAl_6$)/($\alpha + MnAl_6 + \gamma$) boundary extends from $MnAl_6$ (with silver in solid solution)

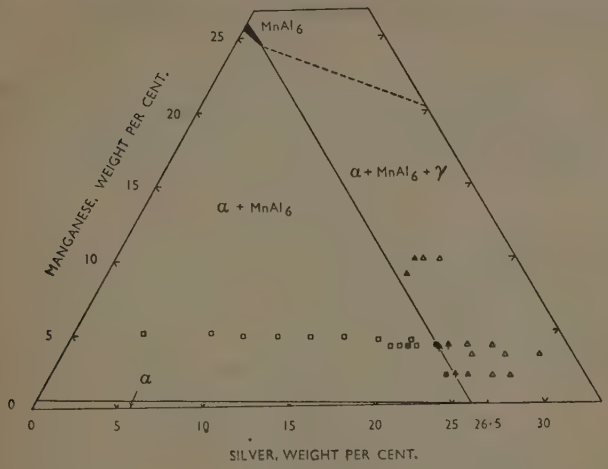

FIG. 15.

	Analysed.	Unanalysed.
$\alpha + MnAl_6$	■	□
$\alpha + MnAl_6 + \gamma$	▲	△
Traces of third phase	↟	

to a composition of 25·5% silver on the aluminium–silver axis. This composition is somewhat less than the solubility limit of silver in aluminium (26·5%) at this temperature.

5. *Slowly Cooled Alloys.*

Three alloys, containing 4% manganese and 5, 10, and 15% silver, respectively, were slowly cooled from the liquid state at a controlled rate of 1·5° C./min. All three alloys contained large primary crystals which were identified by their etching characteristics as $MnAl_6$, together with smaller secondary crystals of $MnAl_6$ and the aluminium–silver γ phase. In alloy 4/15, some of the $MnAl_6$ crystals contained small cores of $MnAl_4$. The primary crystals from alloy 4/10 were extracted electrolytically by anodic solution of the matrix in 10% aqueous nitric acid. Analysis of a clean, hand-sorted sample of the needle-shaped primary crystals obtained showed them to contain 1·69 wt.-% silver and 24·7 wt.-% manganese, confirming that they were correctly identified as $MnAl_6$ crystals. Further confirmation was obtained by comparing the X-ray diffraction pattern of these crystals with that of $MnAl_6$. The

analysed sample was clean and of good quality, and it is most unlikely that the silver content could have arisen by contamination of the residue with matrix material. There is, therefore, a solubility of silver in $MnAl_6$, extending up to 1·69%.

No micrographic constituents other than α, $MnAl_6$, and γ were observed in the micro-sections of these alloys, and no crystals of habit different from that of $MnAl_6$ were detectable in the extracted residue. The experiments therefore confirm the absence of a ternary compound in equilibrium with the primary solid solution in this system.

6. *Summary.*

Experiments on slowly cooled aluminium–manganese–silver alloys, and on annealed and quenched solid alloys, show that equilibrium in the aluminium-rich region involves only α, $MnAl_6$, and the γ phase of the aluminium–silver system. The region of the isothermal diagram at 495° C. in which α is in equilibrium with $MnAl_6$, which can hold 1·69% silver in solid solution, is extensive (Fig. 15).

IV.—Discussion.

The work described in the foregoing sections establishes that, whereas a ternary compound with an electron : atom ratio of 1·85 and with a ratio of 4 aluminium atoms to 1 solute atom occurs in the aluminium–manganese–copper system, the substitution of silver for copper causes the non-appearance of such a compound. The system aluminium–manganese–zinc contains such a compound, but the system aluminium–manganese–magnesium contains a ternary compound which is of a different type, with an electron : atom ratio of 2·37. It is of interest to consider the composition of the compound $T(MnMg)$ in more detail.

According to the work of Little, Axon, and Hume-Rothery,[22] the system aluminium–chromium–magnesium also contains a ternary compound (E), which has a relatively wide range of homogeneity. This compound was recognized by Erdmann-Jesnitzer,[23] who suggested that its composition could be represented by the formula $CrMgAl_8$. Analysis of the extracted ternary-compound crystals obtained in the more recent work, however, showed that the composition could be better represented by the formulæ $Cr_2Mg_3Al_{25}$ (2 samples) or $Cr_2Mg_4Al_{24}$ (1 sample), while the results of micrographic work indicated that the range of compositions $Cr_2Mg_3Al_{25}$ to $Cr_2Mg_{4\cdot5}Al_{23}$ is permissible. The electron : atom ratios corresponding to these formulæ are :

$Cr_2Mg_4Al_{24}$:	2·36	electrons per atom.
$Cr_2Mg_3Al_{25}$:	2·39	,, ,, ,,
$Cr_2Mg_{4\cdot5}Al_{23}$:	2·33	,, ,, ,,

Although the homogeneity range includes the composition $(Cr.Mg)Al_4$, this compound cannot be considered as analogous to those occurring in the alloys of aluminium and manganese with copper, nickel, and zinc, in view of the high value of the electron : atom ratio.

It is particularly to be noted, however, that the electron : atom ratio for the ternary phase *T*(MnMg) is included in the range of electron : atom ratios for the aluminium–chromium–magnesium *E* phase. Further, the homogeneity range of the *E* phase can be represented as $(Cr.Mg)Al_{3\cdot54}$ to $(Cr.Mg)Al_5$, while the determined composition of *T*(MnMg) may be represented as $(Mn.Mg)Al_{3\cdot3}$. In view of the fact that the ratios of

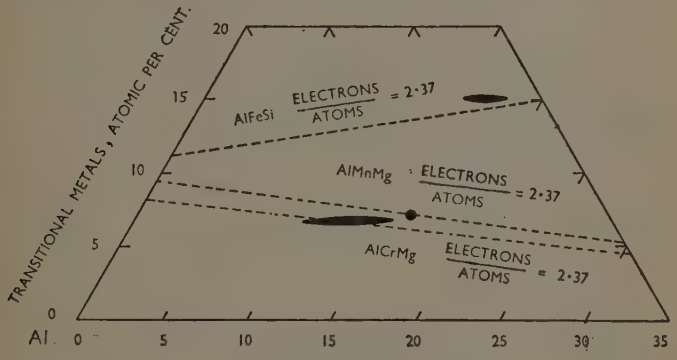

FIG. 16.

transitional metal atoms to magnesium atoms in the two structures are similar, it is probable that the aluminium–chromium–magnesium *E* phase and *T*(MnMg) are to be regarded as analogous ternary compounds, with the aluminium content adjusted to preserve an approximately constant electron : atom ratio.

Recent work in this laboratory has shown that the ternary phase β(Fe–Si) * which occurs in the system aluminium–iron–silicon, also has an electron : atom ratio of approximately 2·32, and it appears probable that this forms a third member of the same group of ternary compounds. The relationship between the three ternary phases is shown in Fig. 16.

Thus, in ternary aluminium-rich alloys with two transitional metals, or with one transitional metal and a non-transitional metal, ternary compounds of at least two types may be formed. In other cases, no ternary compounds are formed. The occurrence and type of the

* The nomenclature used is that of Phillips and Varley.[24]

ternary compound may be expected to be influenced by the size relationships between the constituent atoms. It is of interest to consider this aspect more closely.

It has frequently been pointed out that, in problems of alloy formation, the size of an atom cannot be expressed in terms of a single constant, but that the size of the underlying ion must also be taken into consideration.[25] Accordingly, in Fig. 17, both the interatomic

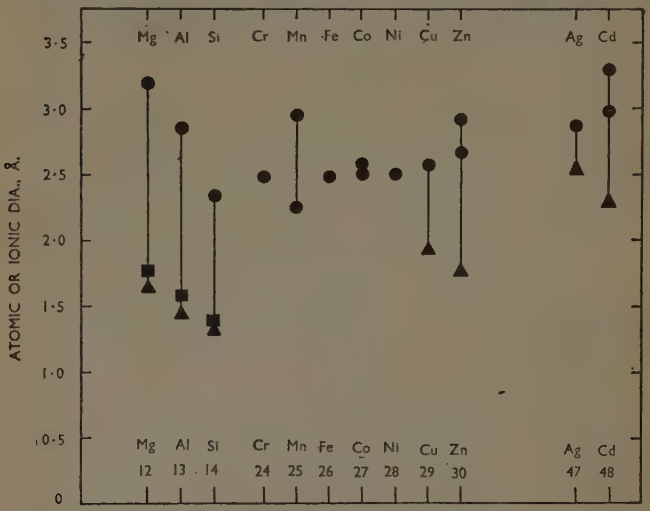

FIG. 17.

● Interatomic distance in crystal.
■ Zachariasen ionic diameter.
▲ Pauling ionic diameter.

distances in the crystals of the elements, and the univalent ionic diameters from the work of Pauling [26] and of Zachariasen,[27] have been plotted for a number of metals. The univalent ionic diameters of Pauling and Zachariasen express the relative extension in space of ions under the influence of a standard force field, and give a relatively close approximation to the sizes of ions in metallic structures.

It will be noted that nickel, copper, and zinc, which respectively form with aluminium and manganese ternary compounds of electron : atom ratio 1·85 with a ratio of aluminium to solute atoms of 4 : 1, have atomic

and ionic diameters which are closely similar. The third metals silver and cadmium, however, whose atomic and ionic diameters are both appreciably larger than those of copper and zinc, do not form ternary compounds with aluminium and manganese. Magnesium, with a relatively large atom, and silicon, with a relatively small atom, both form ternary compounds of electron : atom ratio other than 1·85 with aluminium and manganese. In this case, it will be noted that the ionic diameters are relatively small.

On the evidence at present available, therefore, it would appear that, for the formation of a ternary compound of electron : atom ratio 1·85, the atomic and ionic diameters of the third metal should be similar to those of copper and zinc. Ternary compounds are not formed if both the atomic and ionic diameters of the third metal are greater than this range, but appear to be capable of existence at electron : atom ratios other than 1·85 if the ionic diameters are appreciably smaller than those for copper and zinc. Similar considerations to those outlined here would be expected to apply to aluminium-rich alloys containing transitional metals other than manganese. The available data are at present too fragmentary for this conclusion to be tested, but, in this connection, the analogy between the ternary phases in the systems aluminium–manganese–magnesium and aluminium–chromium–magnesium is of much interest.

Chromium, iron, and cobalt lie within the favourable zone of atomic sizes for the formation of the ternary compound of electron : atom ratio 1·85. A compound of this type is, however, not found in equilibrium with the primary solid solution. In the case of chromium, this is due to the fact that, at the required ratio of aluminium to solute atoms, the electron : atom ratio 1·85 cannot be obtained. In the case of the aluminium–manganese–iron system, a very extensive solid solution of iron in $MnAl_6$ is formed, probably at the expense of the formation of a ternary compound. There is also a limited solid solubility of manganese in $FeAl_3$. The non-appearance of a ternary compound in equilibrium with the primary solid solution in the aluminium–manganese–cobalt alloys is probably due to the tendency of an atom of cobalt and an atom of manganese to behave similarly to two atoms of iron, just as an atom of iron and an atom of nickel behave similarly to two atoms of cobalt. This would lead to the formation of a compound $MnCoAl_8$, analogous to $FeAl_3$; since such a compound would contain much less aluminium than $MnAl_6$ and Co_2Al_9, it would probably not enter into equilibrium with the primary solid solution.

The results obtained in this work add further support to the theory that, in alloys with aluminium, transitional metal atoms absorb electrons

to the full extent permissible by the vacancies in their atomic orbitals. It is also established that the occurrence of intermediate phases of the type considered here is markedly dependent on the electron : atom ratio, which suggests that such phases are to be considered as analogous to the electron compounds which occur in other, better-known alloy systems.

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EFFECT OF MELTING CONDITIONS ON THE SPECTROGRAPHIC DETERMINATION OF COPPER IN LEAD ALLOYS.*

1149

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Synopsis.

An accurate and convenient method is described for preparing lead–copper alloy standards for spectrographic analysis. The method involves heating the surface of molten metal directly with a coal-gas flame, which dispels the oxide present and enables solid copper to dissolve more rapidly than usual in lead alloys.

The preparation of a number of lead–tin–copper alloys and lead–tin–antimony–copper alloys, and the spectrographic check of these alloys, are described. The concentration–calibration curves obtained are given; these also show the effect of the presence of small amounts of antimony on the determination of copper.

Different methods of preparing routine samples of lead–copper alloys for spectrographic analysis have also been studied.

I.—Introduction.

In the early days of quantitative spectrographic analysis, the standards to be employed were usually obtained by selecting certain samples which had been specially or carefully analysed by the conventional chemical methods in use at the time; they were generally wet methods. In those days the chemist's figure was usually more reliable than the figure obtained by the spectrograph. Recently in a number of instances the spectrographic method has been the means of demonstrating errors, hitherto unsuspected, inherent in the wet chemical methods which had been employed.

Various attempts have been made to counteract errors likely to arise as a result of error in a chemical method. For instance, Darrah, McClelland, and Smith [1] assigned to their standard alloys values which were the averages of independent analyses carried out by members of the British Standards Institution Panel which organized the investigation in question. Before the average values were adopted, spectrographic checks were made " by independent determinations of the contents by reference to the mean calibration curves obtained by

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methods which each member regarded as giving the best accuracy". This procedure would probably minimize experimental error, but might not avoid an error inherent in the chemical method unless a variety of different methods were employed by the several analysts who participated in the work.

Kingsbury and McClelland,[2] examining high-purity zinc and alloys of zinc, claimed the spectrographic method to be "certainly capable of a greater degree of accuracy than chemical methods" for the elements lead and cadmium. For evaluating their standards they preferred the polarograph rather than wet chemical methods. Some of the standards used by Kingsbury and McClelland [3] were given values based on "the amount of impurity added at the time of manufacture of the samples".

The British Non-Ferrous Metals Research Association's Panel No. 3 working on the analysis of lead recommended that standards should be prepared by melting together in evacuated glass tubes (Pyrex or Monax) accurately weighed quantities of the constituent metals and then checking spectrographically before their adoption.[4]

There were reasons for seeking an alternative method, namely (*a*) temperatures in the region of 600°–700° C. have been found desirable for the making up of lead alloys containing copper, and longer times are necessary than for most alloys in use; this increases the difficulties when using glass; (*b*) much larger amounts of alloys are required than can conveniently be prepared in glass tubes.

An improved method has been developed and is put forward because it is considered to be more convenient for making up large amounts of standards and also because it is more accurate. A part of the technique employed was suggested as a result of observing some effects of flames impinging directly on molten lead.

II.—Action of Flame on Molten Lead.

It was observed that if solid dross were floating on molten lead it could be caused to shrink very considerably in volume and apparently almost disappear when an oxidizing flame from a Bunsen burner fed with coal-gas was played directly on it. It was further observed that if the flame was made to continue to play on either molten lead or its alloys containing tin and antimony, or tin and copper, the result was that a certain area of the molten metal became entirely free from any visible surface film or skin, such as oxide, which always forms under ordinary conditions. The film-free area had a mirror-like appearance. The direct action of a flame on ores is utilized in smelting, but the impinging of a flame on molten metals during remelting, as for casting, is usually carefully avoided because it introduces porosity due to gas dissolving in

the metal. This is especially the case with copper, aluminium, and steel, but it does not seem to cause porosity in the case of lead. On the contrary, it has a beneficial result.

During observations on the effect of varying the proportions of oxygen and of coal-gas in a flame impinging on B.H.A.S. lead it was found that a film forms both with excess oxygen and also with excess gas. However, when air was used in the proportion which produces the well known two-cone non-luminous roaring Bunsen flame, the film disappeared, leaving a bright mirror of molten lead where the flame touched it. It was also found that by placing the Bunsen burner so that the tip of the flame's inner cone occasionally licked the mirror surface, little patches of brightly coloured films were formed which floated away from the flame and then apparently disappeared. By fixing the burner still nearer the molten metal it was possible to produce several orders of interference colours, and ultimately the centre of the coloured patches wrinkled, showing that there was a film of appreciable thickness at this position.

The temperature which the metal reached also had an effect. At a certain stage during a steady rise in temperature the surface film was obviously solid, but it later altered markedly in appearance, resembling first the breaking up of ice-floes which soon apparently melted over a circle with its centre at the position of the flame. The difference in appearance between solid film and molten film floating on the top of the lead was quite appreciable. By fixing the Bunsen burner so that the flame played on only one half of the exposed surface, it was possible to have a solid oxide film on one side showing characteristic interference colours and a greyish film—more sensitive to chance movements and probably a liquid film of oxide—on the other side of the pool of lead, with a mirror in between the two.

It was decided to attempt to utilize this film-free area for the alloying of copper and lead, and it was found that copper dissolved in lead more rapidly under these conditions than when the lead was heated in the normal manner. This techique was therefore used to prepare a series of lead–copper standards. In doing this the lead and also the copper were accurately weighed. Furthermore, by weighing the final alloy, taking into account all relevant weights, and also determining, in this case chemically, the composition of the small amount of dross which remained after casting the metal, it was possible to calculate with little error the copper content of the alloy. The restricted use of wet chemical methods was considered quite legitimate because only an abnormally large error in this would significantly affect the final result.

Two sets of alloys were prepared, one set containing 0·1% tin, the

other set containing 0·4% tin and 0·2% antimony. Four standards were prepared for the tin series containing the following nominal amounts of copper: 0·035, 0·045, 0·055, and 0·065%. Five standards were prepared for the tin + antimony series; the copper contents in this case were nominally 0·020, 0·035, 0·050, 0·065, and 0·080%.

III.—Preparation of the Standards.

1. *Technique.*

A definite amount of B.H.A.S. lead (weighed to 0·01 g.) was melted in an iron ladle. Heating was then continued by directing an air/coal-gas flame on to the molten surface until the temperature was 700° C. An ordinary Bunsen burner was used with the air-inlet port set to give a two-cone non-luminous roaring flame. This in contact with the surface appeared to reduce most of the oxide which had formed during melting and produced a brilliant mirror-like surface. When this stage was reached, a known amount of pure tin (weighed to 0·0001 g.) was added, the alloy was mixed and the heating with the flame continued. When the mirror-like surface had re-appeared, a known amount (weighed to 0·0001 g.) of 0·01-in. copper strip (cut into small pieces) was brushed from the watch glass on which it had been weighed on to the surface. The heating was continued until all the small pieces of copper had disappeared; this took about 20 min. The metal was then well mixed by stirring it with a nickel spatula, cast into flat spectrographic test-pieces (10 × 3½ cm. × 3 mm.) and weighed. The dross remaining in the iron ladle and on the spatula was weighed, transferred directly to a glass beaker, and chemically analysed for copper, tin, and lead contents.

The lead–tin–antimony–copper standards were prepared in exactly the same way as for the above-described series except that there was also the addition of a calculated weight of 10% lead–antimony alloy before addition of the copper.

Details of the preparation of one standard are given below.

Weight of lead	999·65 g.	Weight of alloy	996·77 g.
Weight of tin	0·9995 g.	Weight of dross	4·2233 g.
Weight of copper	0·3500 g.		
	1000·9995 g.		1000·9933 g.

Chemical Analysis of Dross.

Lead	4·1420 g.
Tin	0·0157 g.
Copper	0·0025 g.
	4·1602 g.

From the foregoing, 996·77 g. of alloy contains (0·3500–0·0025) g. of copper = 0·3475 g. Therefore the copper content is 0·0349%.

The difference between the observed weight of the dross, namely 4·2233 g., and the total weight derived by chemical analysis of lead+tin + copper, namely 4·1602 g., is very probably due to oxygen uptake. The total metal unaccounted for gravimetrically during the whole of the operations described was 1000·9995 − (996·77 + 4·1602) = 0·069 g., i.e. less than 0·007% of the weight of the standard produced. Much importance is attached to the over-all change in weight during the preparation of one of these special standards. Comparisons of the sum of the weights of alloy and dross with the sum of the weights of all component metals showed that there was usually a small loss recorded, but occasionally a gain. In Table I are collected the changes in weight during the making of the nine standards.

TABLE I.

Series.	Copper, %.	Difference in weight in proportion to total weight of alloy, %.
Lead–tin . . .	0·035	−0·006
,, . . .	0·045	−0·010
,, . . .	0·055	−0·016
,, . . .	0·065	−0·012
Lead–tin–antimony . .	0·020	−0·006
,, . .	0·035	+0·004
,, . .	0·050	−0·003
,, . .	0·065	+0·024
,, . .	0·080	+0·015

The over-all difference in weight, during the alloying of all the above-quoted standards, is lower than 0·025%—the allowance in the method previously recommended.[4]

To ascertain whether any loss due to volatility occurred, 1000 g. of lead was weighed, heated for 20 min. after becoming molten, allowed to cool and reweighed, but no loss in weight was recorded.

2. *Spectrographic Check of Composition.*

Triplicate exposures of each standard were photographed on the same plate, using a Hilger medium spectrograph (E3). The light source was a simple condensed spark, of voltage 15,000, capacity 0·0125 μF., and self-inductance 0·13 mH. A 3-mm. spark was focused within the optical system of the spectrograph by means of the quartz lens F 1026. The duration of exposure was 15 sec.; there was no pre-spark. The lines measured, using a Hilger non-recording microphotometer,

were copper 3273·9 A and lead 2628·3 A. The logarithms of the ratio of the galvanometer deflections given by these lines plotted against the logarithms of the copper percentages are shown in Fig. 1. A linear

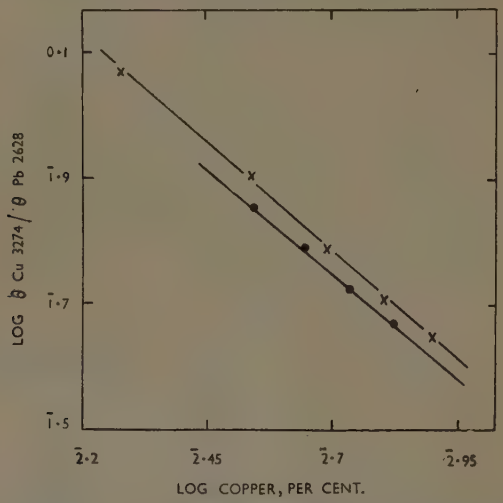

FIG. 1.—Calibration Curves for Lead–Tin–Copper Alloys and Lead–Tin–Antimony–Copper Alloys.

● Lead–tin–copper alloys.
× Lead–tin–antimony–copper alloys.

relationship was obtained for the four standards of the lead–tin–copper series, and for the five standards of the lead–tin–antimony–copper series. This result is a further indication that the method employed for the preparation of the standards was satisfactory, and it has been adopted for the preparation of all lead–copper alloy standards.

3. *Effect of Antimony on the Determination of Copper.*

The concentration–calibration curves also show the effect of the presence of antimony on the determination of copper in lead. It can be seen that if the copper contents of samples containing antimony are determined by reference to antimony-free standards, the results obtained will be low. The error caused would be between 10 and 12% of the copper content. Thus, for this method to be used successfully the antimony contents of the standard alloys must be very close to those of the samples for analysis.

4. *Preparation of Other Standards.*

While the use of the flame directly on the metal was restricted to the lead alloys containing copper, the technique of adding accurately weighed quantities of components to accurately weighed amounts of

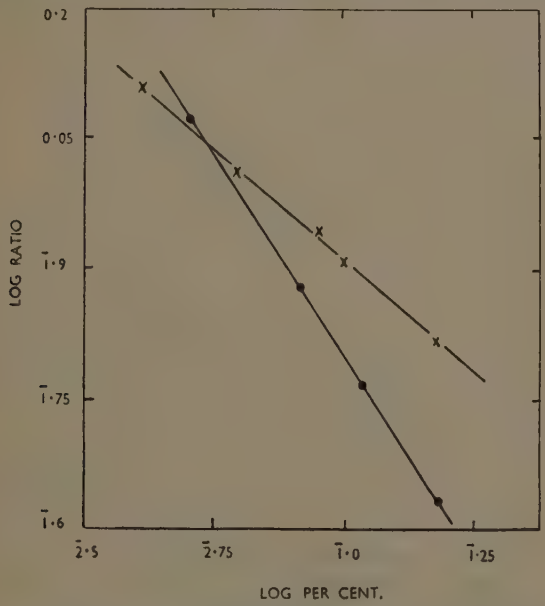

Fig. 2.—Calibration Curves for Lead–Tin and Lead–Antimony Alloys.
● Lead–tin alloys.
× Lead–antimony alloys.

lead was used for the preparation of lead–tin alloys, lead–antimony alloys, and lead–tin–antimony alloys. The method again proved satisfactory, and the concentration–calibration curves are shown in Figs. 2 and 3. The lines used were lead 2628·3 A, tin 2706·5 A, and antimony 2598·1 A.

IV.—Effect of Different Methods of Preparation of Samples.

1. *Effect of Casting Conditions.*

Usually, test-pieces of lead alloys for spectrographic analysis have been prepared by heating the sample to the lowest temperature con-

sistent with the making of a good casting. Many samples containing copper have been analysed, and at times there have been apparently large variations in the copper content of the same sample. The following experiments were carried out in order to find the best conditions for preparing test-pieces of lead alloy samples. At the same time experi-

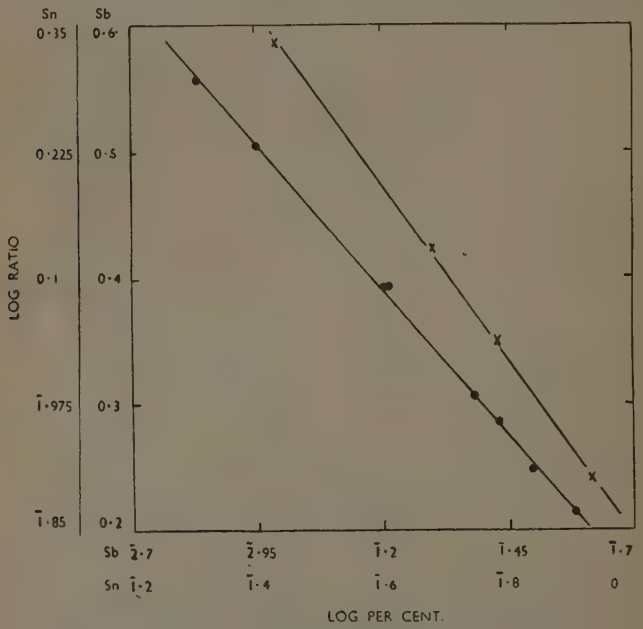

FIG. 3.—Calibration Curves for Lead–Tin–Antimony Alloys.
× Antimony.
● Tin.

ments were performed to find out whether segregation occurs in the casting as normally used for analysis.

For the following experiments a 1-cwt. pig of lead–tin–antimony–copper alloy, which had been made from scrap lead, was obtained. The effects of melting conditions on the derived copper figure and the distribution of the copper figures were first studied. A piece of alloy 1000 g. in weight was cut from the pig and melted in an iron ladle over a gas-ring flame. When the temperature had reached 350° C. a casting was made for spectrographic analysis, the iron mould being at about

100° C. (test-piece 1). The copper content varied from 0·033 to 0·035%, except at the bottom of the casting, where it reached 0·054%. This is shown by reference to Fig. 4 and Table II.

The alloy which remained in the ladle after the casting of test-piece 1 was heated to 600° C.; a second casting was then made (test-piece 2) (Table II). A general increase in copper content was found, namely to 0·061–0·069%.

The metal which still remained in the ladle after the casting of test-piece 2 was allowed to cool to about 350° C. and then reheated to 600° C., this time using the flame technique, described above, to produce a mirror-like appearance. A further casting was then made (test-piece 3) (Table II). The copper content increased again, to 0·076–0·085%.

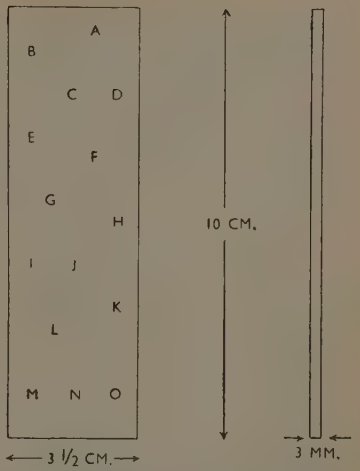

FIG. 4.—Sketch of Test-Piece Showing Positions Where Analyses Were Made.

2. *Effect of Rolling on the Analysis.*

The following experiments were made to find out whether casting the alloy into stick form, followed by rolling to the desired thickness, gave more reproducible results than the ordinary casting method.

A piece of alloy was cut from the same pig as before and melted over a gas-ring flame, at 350° C. Two sticks, each $18 \times \frac{1}{2} \times \frac{3}{8}$ in., were cast, using an open multiple-stick mould in a horizontal position at about 100° C. The remaining alloy was subjected to the flame technique, and another two sticks were then cast. The alloy still remaining was cast into button form; when solid it was remelted over a gas-ring flame and cast at 350° C. into a further two sticks.

One stick of each sample was next rolled to a long narrow strip of thickness 3 mm., giving test-pieces 4, 5, and 6; these were then cut so that 14 or 15 exposures of each could be made at positions distributed throughout their lengths. The results are given in Table III. The effect of the special flame treatment was again marked, the copper content being 0·070–0·082% after the treatment, as compared with

TABLE II.

Position shown in Fig. 4.	Test-Piece 1. Cast at 350° C.	Test-Piece 2. Cast at 600° C.	Test-Piece 3. Cast at 600° C. after treatment with Bunsen flame.
	Copper, %.	Copper, %.	Copper, %.
A	0·034	0·061	0·076
B	0·034	0·065	0·076
C	0·034	0·062	0·085
D	0·034	0·066	0·078
E	0·034	0·066	0·077
F	0·033	0·062	0·082
G	0·034	0·062	0·081
H	0·035	0·061	0·077
I	0·034	0·066	0·080
J	0·034	0·069	0·082
K	0·034	0·067	0·084
L	0·034	0·068	0·083
M	0·040	0·066	0·081
N	0·045	0·064	0·081
O	0·054	0·063	0·084
	Tin, %.	Tin, %.	Tin, %.
Maximum	0·33	0·35	0·37
Mean	0·32	0·34	0·36
Minimum	0·30	0·33	0·34
	Antimony, %.	Antimony, %.	Antimony, %.
Maximum	0·32	0·31	0·32
Mean	0·29	0·29	0·29
Minimum	0·26	0·27	0·28

0·038–0·042% before the treatment. The effects of the various methods of preparation are summarized in Table IV.

V.—Discussion of Results.

From the results given above, it is deduced that lead alloys for spectrographic analysis must be heated to 600°–700° C. in order to obtain a true copper figure. The best method of heating known to the authors consists in directing a coal-gas/air flame from a Bunsen burner downwards on to the surface of the alloy. The heating should be continued until the alloy shows a mirror-like surface; this occurs after the temperature has reached about 600°–700° C.

The increase in copper content as a result of this flame treatment on the surface was accompanied by a small increase in the tin content. The antimony was scarcely affected by these different methods of heating. Test-pieces obtained by rolling cast sticks gave similar results to the as-cast test-pieces. The samples rolled from the stick castings showed somewhat better agreement than did the as-cast test-pieces. The difference in copper content among 14 samples cut from one

TABLE III.

Sequence along Strip.	Test-Piece 4. Sticks cast at 350° C. then rolled to 3 mm.	Test-Piece 5. Sticks cast after treatment with Bunsen flame then rolled to 3 mm.	Test-Piece 6. Re-cast at 350° C. into sticks after treatment with Bunsen flame then rolled to 3 mm.
	Copper, %.	Copper, %.	Copper, %.
1	0·038	0·081	0·080
2	0·041	0·080	0·082
3	0·039	0·081	0·082
4	0·042	0·078	0·079
5	0·041	0·078	0·070
6	0·040	0·081	0·076
7	0·040	0·080	0·077
8	0·042	0·081	0·072
9	0·040	0·081	0·073
10	0·040	0·080	0·071
11	0·040	0·081	0·071
12	0·041	0·081	0·073
13	0·041	0·082	0·070
14	0·041	0·082	0·071
15	0·039	...	0·070
	Tin, %.	Tin, %.	Tin, %.
Maximum	0·32	0·36	0·40
Mean	0·31	0·34	0·38
Minimum	0·31	0·34	0·36
	Antimony, %.	Antimony, %.	Antimony, %.
Maximum	0·31	0·32	0·33
Mean	0·30	0·31	0·31
Minimum	0·28	0·30	0·29

TABLE IV.

Test-Piece Number.	Conditions of Casting.	Form of Test-Piece.	Limits of Range, Copper Content, %.
1	350° C.	As cast	0·033–0·054
2	600° C.	,,	0·061–0·069
3	600° C. after flame technique at 600° C.	,,	0·076–0·085
4	350° C.	Stick, rolled	0·038–0·042
5	700° C. after flame technique at about 700° C.	,,	0·078–0·082
6	350° C. after flame technique at about 700° C. and solidifying	,,	0·070–0·082

rolled strip was 0·004%, as compared with 0·008% among 15 samples cut from a cast test-piece.

The only casting which showed any marked segregation was test-piece 1, cast at 350° C., the bottom of this casting being rich in copper. This is taken to be due to the alloy from the bottom of the spectro-

graphic mould coming from the top of the molten alloy; this was rich in copper.

The remelting and casting at 350° C. of a sample which had previously been heated on the surface with a Bunsen flame to about 600°–700° C. and allowed to solidify, gave much better results than the casting of samples in the ordinary way at 350° C. This suggests that the treatment had resulted in the copper present in the alloy becoming more uniformly distributed. Casting at 700° C. gave still higher results. Presumably, the lower results after casting at 350° C. were due to the floating of copper-rich material to the surface during melting and before casting.

Acknowledgements.

The authors wish to express their indebtedness to the Directors of British Insulated Callender's Cables, Ltd., for permission to publish this work, and also to their colleagues Mr. R. Rimmer, who carried out all the chemical analyses, Mr. A. King and Dr. A. Latin, with whom discussions were held which led to this work being commenced.

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THE FLOW OF METAL IN TUBE EXTRUSION.* 1150

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Synopsis.

Experiments on billet flow were carried out in a 600-ton vertical tube-extrusion press of Schloemann make and a 1000-ton press of Loewy make. Flow was studied by means of small pins inserted in the outside of the billets and by means of composite billets. The principal factor determining the type of flow is the degree to which the skin of the billet remains in place against the container wall. In a non-lubricated container, there is sufficient friction between brass and copper–nickel billets and the container wall to hold the skin of the billet in place, but with copper the oxide envelope formed in pre-heating appears to function as a lubricant for the underlying metal. In a lubricated container, brass and copper–nickel flow like copper. When copper is prevented from oxidizing it flows like brass in a non-lubricated container, and when a layer of copper is placed around a brass billet the brass flows in a non-lubricated container in the same way as copper.

The presence of a thick oxide layer, *per se*, is not a guarantee that the billet will exhibit the lubricated type of flow; the controlling factor appears to be whether or not the billet can slide within its oxide envelope under pressure in the container.

The structure of the skull left in the container at the end of extrusion was studied microscopically. So distinctive are the features of skulls that they can be relied on to indicate the nature of flow in the billet.

The structure of the plug pushed out by the mandrel in the early stages of extrusion was also studied.

The relationship between different portions of the billet and different portions of the extruded shell was established for the two principal types of flow.

I.—Introduction.

The hydraulic extrusion presses that are used in copper and brass tube mills to produce hollows for tube-drawing operations are employed exclusively in some mills on copper alloys, such as brass and copper–nickel, but in others they are regarded as useful complements to rotary piercers for the production of some sizes of copper tubing, despite the comparatively high cost of operating them.

A comprehensive review of most aspects of extrusion was published by C. E. Pearson [1] in 1944, and a brief description of some features of copper alloy tube extrusion by W. L. Govier [2] in the same year. With

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this information available it might be thought that there is little to add to the subject, but the present authors have found difficulty in picturing the flow of copper and copper alloys in vertical tube-extrusion presses from information so far published and have been led to carry out further work in an attempt to elucidate a number of unexplained points.

In this paper a description is given of experiments on copper and copper alloys in a 600-ton vertical press made by Schloemann of Düsseldorf in 1934 and a 1000-ton vertical press made by the Loewy Engineering Co., London, in 1943–44. Both presses were of standard type when purchased by Metal Manufactures, Ltd. There has been no opportunity of carrying out experiments in horizontal presses or in vertical presses of a design different from those just mentioned.

II.—The Tube-Extrusion Process.

Although the practical details of extrusion are well known to those who are engaged in the copper and brass tube industry, a brief description of the successive stages in the extrusion of tubes in presses of the type mentioned above is necessary here to define terms and provide a key to the drawings that have been used to illustrate the results of the experiments.

Billets for extrusion are 6–12 in. long, 4·7–7·2 in. dia., and 39–117 lb. weight, depending on the size of press, the composition of the alloy used, and the dimensions required in the extruded shell. They are obtained by sawing long, vertically cast billets into the required length. In some tube mills, the as-cast billets are turned in a lathe to remove surface defects, and the short billets obtained from them are sometimes bored to remove axial porosity, lighten the strain on the piercing mandrel, and reduce the tendency to produce eccentric shells; but, unless otherwise stated, the experiments to be described were made with unturned, unbored billets.

The first stage in extrusion is to place a hot billet upright on the die in the press container, followed by a pressure disc or pad on top of the billet (Fig. 1(*a*)). The stem of the press, with the mandrel in the partly extended position to fill the central hole in the disc, is next lowered gently to expand or upset the billet to meet the container wall. The stem is then withdrawn slightly and the billet pierced by the mandrel (Fig. 1(*b*)). A solid plug of metal is pushed downwards from the die by this operation and is, of course, unavoidable scrap. Then, without pause, stem and mandrel are together brought down at full pressure to force the billet through the annular space between die and mandrel as a hollow or shell (Fig. 1(*c*)). When about 0·25 in. of

billet remains, the press is stopped and the stem and mandrel withdrawn to allow the shear ring or cutter, on which the die has been supported, to be moved across to cut off the suspended shell (Fig. 1(*d*)).

The term " shell " is commonly used to denote the extruded product so as to avoid confusion with the term " tube ", which is reserved for the finished product made by subsequent cold drawing.

At this stage the container holds the die, the disc, and a residue of metal composed of a thin hollow cylinder against the container wall and a thin piece of unextruded billet between die and disc to which is

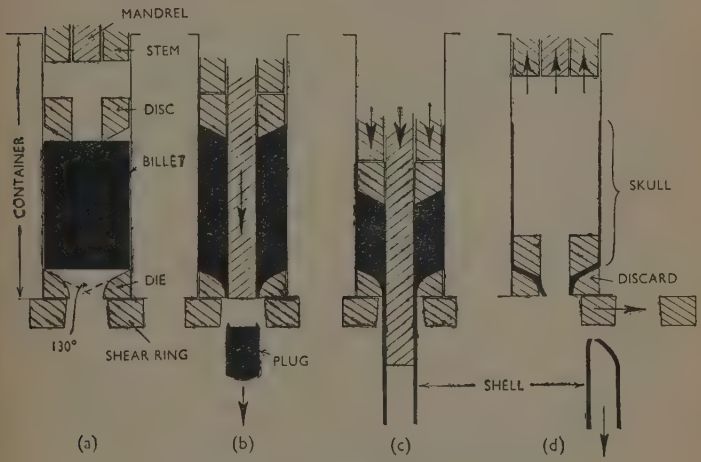

FIG. 1.—Successive Stages in Tube Extrusion.

attached a short piece of shell in the throat of the die. The thin cylinder is purposely made by the use of a disc smaller in diameter than the inner diameter of the container. It varies in thickness from less than 0·01 in. to about 0·05 in.

The final operation is to remove die, disc, and residue by means of the stem and a close-fitting cleaning pad.

The term " discard " will be used to denote the metal left between die and disc, and the term " skull " to denote the thin hollow cylinder left against the container wall. Under the conditions just described, skull and discard, although joined together at the completion of the extrusion stroke, are usually ejected from the container as separate pieces. Like the plug, they are scrap.

Whenever, in the course of the experiments, it was deemed necessary

to study the structure of a skull, it was lifted out with tongs from the top of the container instead of being pushed out by a cleaning pad. By this means, crumpling of the skull was avoided.

The cutting of a well defined skull has been included in the description as an essential part of extrusion so that departures from assumed standard practice can be readily explained.

III.—Plan of Experiments.

In the experiments to be described, the following conditions were observed unless otherwise stated. Die, mandrel, and side of disc were lubricated for each extrusion, but the under or sloping face of the disc and the wall of the container were not lubricated. The billet was partly or wholly extruded, depending on whether early, intermediate, or late stages of flow were to be studied. Vertical (i.e. radial) sections of discards were polished and etched for macroscopic examination, and vertical (i.e. longitudinal) sections of skulls were prepared for microscopic examination. Cross-sections of shells were cut at various places, and vertical (i.e. longitudinal) sections of plugs were prepared when deemed necessary. Billet temperature varied from about 675° C. for 60 : 40 brass to about 1000° C. for 70 : 30 copper–nickel. The sloping face of both disc and die was constant throughout at an angle of 25° to a horizontal plane, i.e. an included die angle of 130°. Billets extruded in the 600-ton press were pierced with a pointed mandrel, while those extruded in the 1000-ton press were pierced with a square-ended or blunt mandrel. The lubricant was composed of a mixture of graphite and a proprietary grease.

Extrusion pressure and time for extrusion were not consistently recorded; in normal working they are functions of billet alloy, size of shell, and precise method of lubrication. Nor was the temperature of the container measured. It probably varied from one experiment to another, but only within what was regarded as a suitable working range. The container was heated externally by means of electric-resistance elements and internally by the hot billets. At both presses the billets were heated in oil-fired furnaces. The experiments as a whole were designed to investigate flow of the metal under normal working conditions. For this reason, no attempt was made to test the effect of not lubricating either the die or the mandrel.

The experiments were spread over a number of years, with many repeat tests. Except for the effect on the plug of differences in the shape of the mandrel (pointed or blunt), similar results were obtained in both the small and the large press.

After trying various methods of following the flow of metal in the container, it was found that the simplest way was to drill shallow holes down the side of the billet, insert metal pins in these holes, and, after extrusion, to section discard and skull through the line of pins. Most experiments were carried out on this basis, but many were carried out on composite billets made by joining together horizontal layers of different alloys.

Holes 0·25 in. dia. and 0·5 in. deep were drilled at regular intervals down the side of a billet at one, two, or three places evenly spaced around the periphery (i.e. one, two, or three lines of holes) and then filled tightly with pins cut from drawn rod 0·25 in. dia. As a rule, five holes were drilled in any one line, but in some instances as many as 26 were used. Exploratory tests with pins inserted in various patterns on top of the billet indicated that a few pins placed diametrically were sufficient to decide the problems at issue in this region. As a rule, pins were not inserted on the bottom surface.

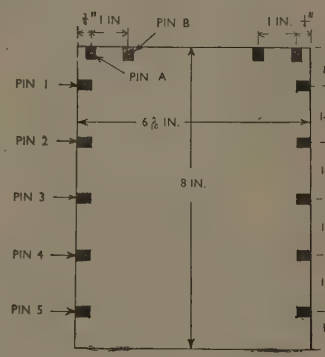

FIG. 2.—Vertical Section Through Billet, Showing Positions of Pins.

Most experiments on brass were made on billets 8 in. long × 6·2 in. dia. weighing 76 lb. for extrusion in the 1000-ton press, and 7 in. long × 4·7 in. dia. weighing 39 lb. for extrusion in the 600-ton press. Copper billets for the 1000-ton press were 9–11 in. long × 6·2 in. dia. weighing up to 108 lb. The effect of mass of billet was unimportant. Copper–nickel billets 6 in. long × 5·125 in. dia. weighing 40 lb. were extruded in the 1000-ton press.

A vertical section through a prepared billet is shown in Fig. 2.

To reduce to a minimum the possible complicating influence of extruding two different alloys at one time, the pins were made of an alloy resembling the billet alloy but differing in a minor constituent that affected etching properties; for example, when experimenting with brass billets containing a small proportion (0·03%) of arsenic, the pins were composed of non-arsenical brass, and *vice versa*; and when extruding deoxidized copper the pins were made of oxygen-bearing (H.C.) copper, and *vice versa*. When the sectioned discards, skulls, and shells were subsequently etched in nitric acid the pins were clearly distin-

guishable from the rest of the section. Pins in 70 : 30 copper–nickel were mild steel.

In studying the structure of a skull, a narrow strip was cut vertically through a line of pins and then rolled into a spiral for convenience in mounting for the microscope. As the length of a skull was many times greater than the thickness (5–12 in. compared with 0·005–0·05 in.), the structure is most conveniently represented by drawings in which thickness compared with length is exaggerated 20 times.

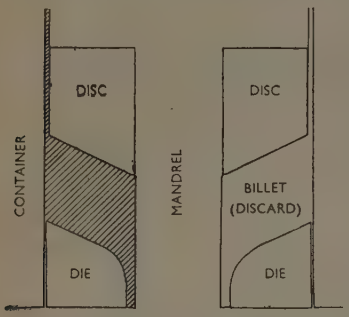

Fig. 3.—Vertical Median Section Through Billet Three-Quarters Extruded, Showing its Relation to Die, Disc, Mandrel, and Container. Details of the hatched portion on the left side are alone necessary to demonstrate the flow of the metal.

It is clear from a glance at Figs. 1 and 3 that, in a pictorial representation of the structure of a discard or skull, there is need only to show one side of a vertical section. In the description of the experiments, the left side shown hatched in Fig. 3 will invariably be depicted. And as black and white drawings, based on tracings of etched structures, are sharp in outline and detail, they will be given in preference to photographs. While photographs are undoubtedly more realistic than drawings, they suffer from the disadvantage that they do not reveal with equal clarity both the smallest and the largest significant details of any one section.

IV.—Flow of Brass in a Non-Lubricated Container.

Under the conditions of lubrication described above, in which the outstanding feature is the non-lubricated container, the normal type of flow for brass of 60 : 40, 65 : 35, 70 : 30, 70 : 29 : 1 (Admiralty brass), and 76 : 22 : 2 (aluminium brass) compositions, as well as for copper–nickel of 70 : 30 composition, is as shown in Fig. 4, where the dark areas are the pins. Side pins 1 to 5 are, as it were, drawn into the interior of the billet and ultimately carried down the die between the walls of the shell in greatly elongated form. As a rule, pin 4 is the first to reach the die, followed by 3, then by 2 and 5, and lastly by 1. Pin 5 does not break through to the outside of the shell but remains with the other pins within the body of the shell. With the top pins there is a movement

towards the mandrel until, near the end of extrusion, pin *B* is well through the die. The extent to which pin *A* moves towards the mandrel depends partly on how close it is inserted to the edge of the original billet. Fig. 12 (Plate XIII) shows the shape and position of side pins 1 to 5 in a cross-section of the wall of a shell after a billet has been

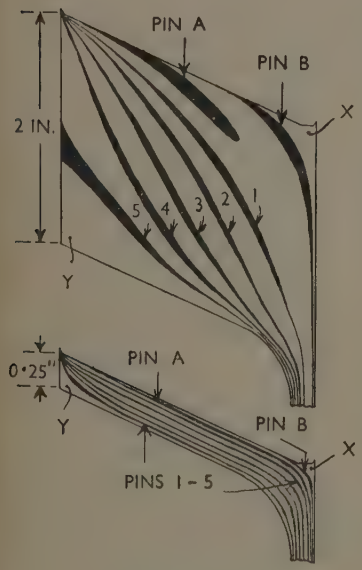

Fig. 4.—Vertical Sections Through Discards of Brass Billets Three-Quarters (*upper*) and Fully Extruded (*lower*) in a Non-Lubricated Container, Showing Manner in which Pins are Drawn into the Billet and down into the Shell.

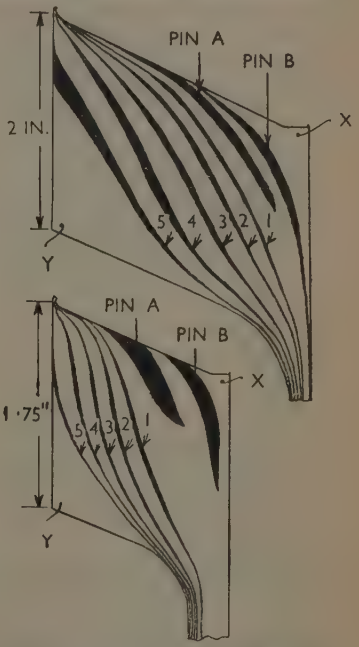

Fig. 5.—Vertical Sections Through Discards of 10 in. Brass Billets Four-Fifths Extruded in a Non-Lubricated Container. (*Upper*) extruded to a shell 2·36 in. external dia. × 1·97 in. internal dia. (60 × 50 mm.). (*Lower*) extruded to a shell 4 in. external dia. × 3·31 in. internal dia.

three-quarters extruded. The section has been cut close to the upper or die end of the shell. Top pin *B* has not yet passed through the die. When, after further extrusion, it does do so, it occupies a position close to the inner wall.

The discards shown in Fig. 4 were made from a billet 8 in. long, the shell being 2·36 in. external dia. × 1·97 in. internal dia. (60 × 50 mm.).

That length of billet and size of shell have no important effect on type of flow is clear from Fig. 5, where the 2-in. discard shown in the upper drawing was made from a billet 10 in. long (with pins proportionately spaced) extruded to a shell 2·36 in. external dia. × 1·97 in. internal dia., and the 1·75-in. discard shown in the lower drawing was made from a similar billet extruded to a shell 4 in. external dia. × 3·31 in. internal dia. For practical purposes, these are close to the extremes in size of shell to be obtained with brass extruded in a 6·25-in. container. The shell in one case was 13 ft. 10 in. long and in the other only 3 ft. 8 in. long. Extrusion was carried out at lower pressure with the large- than the small-diameter shell, the press operator having to throttle the valve for the large shell to avoid over-rapid extrusion.

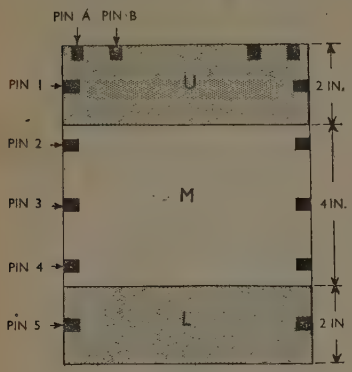

FIG. 6.—Composite Billet : Upper (*U*) and Lower (*L*) Portions Made of One Kind of Brass and Middle (*M*) of Another Kind.

A similar effect can be obtained by varying the composition of the lubricant; for example, billets were extruded with the following types of lubricant for die and mandrel :

(*a*) graphite, sulphur, and Caltex Star cup grease mixed to a paste and applied warm.

(*b*) a Vacuum Oil Company's mixture, containing graphite, grease, and small quantities of other constituents, but no sulphur.

Experience had proved that the addition of sulphur to a graphite–grease mixture produced a fluid lubricant when warm, which reduced the time for extrusion, and that mixture (*b*), if allowed to dry after being applied to the warm die and mandrel, appreciably retarded the rate of extrusion. Billets extruded with (*a*) showed the same kind of flow as those extruded with (*b*).

These results indicate that whatever may be the dimensions of the billet, within practical working limits, or the resistance to flow at the die orifice, again within practical working limits, the principal direction of flow in the billet is diagonally towards the annular space between die and mandrel.

Support for these results is obtained from the extrusion of com-

posite billets made of different kinds of brass joined together as shown in Fig. 6. Suitable combinations are upper (*U*) and lower (*L*) parts of 70 : 30 brass and middle (*M*) of 70 : 29 : 1 or 76 : 22 : 2 brass, or *vice versa*; or, better still, *U* and *L* of non-arsenical brass and *M* of arsenical brass of any one of these types. Typical discards from such billets, three-quarters and fully extruded, are shown in Fig. 7.

The criticism has sometimes been advanced that flow in composite billets may be misleading because of the presence of a junction between different sections and of the different degrees of plasticity of the alloys; but, in the authors' experience, it does not matter how the billet is constructed of different brasses (or, as will be shown later, of different coppers), the flow is always the same for a given method of lubrication and always in keeping with that of billets in which the structure is interrupted by nothing deeper than small superficial pins.

In all these instances, the corners *X* and *Y* (Figs. 4, 5, and 7), especially *Y*, are stationary or dead metal, and rarely, if ever, does the outer layer of the billet, either at the top or sides, fold in across these corners to produce a double or blistered wall on the shell.

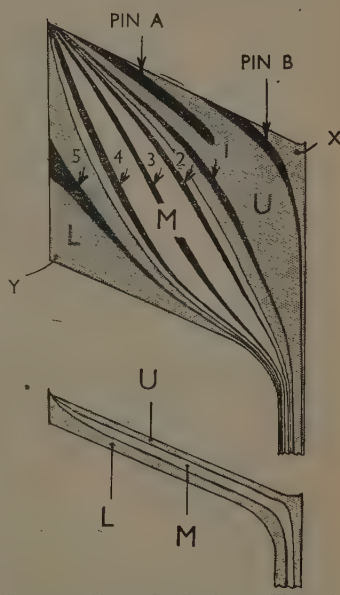

FIG. 7.—Vertical Sections Through Discards of Composite Billets Three-Quarters Extruded and Fully Extruded. The pins have been omitted from the bottom drawing; they occupied positions similar to those shown in Fig. 4 (*lower drawing*), i.e. pins *A*, *B*, and 1 in *U* region; 2, 3, and 4 in *M* region; and 5 in *L* region.

V.—Structure of the Skull.

The outside of the skull of a brass billet extruded in a non-lubricated container is undoubtedly the surface of the original billet, as the heads of the pins are intact and evenly spaced down the outside of the skull, proving that they remain in position, anchored, as it were, to the wall of the container, throughout the whole of extrusion. The inner surface of the skull, which is always smooth and bright from the action of the

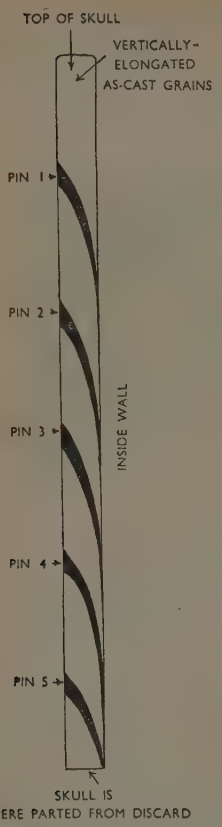

FIG. 8.—Vertical Section Through Skull of Brass Billet Extruded in a Non-Lubricated Container, Showing Positions and Shape of Remnants of Side Pins 1 to 5. Thickness of skull is drawn on a scale twenty times that of length.

disc, is, however, scarcely what one would expect. Considering that the pins are driven 0·5 in. into the billet before extrusion and that the skull after extrusion is usually about 0·03 in. thick, one would expect the pins to be shorn off by the disc close to the heads and to find the greater part of each pin separated from its head at a lower level like the parts of a stratum at a geological fault; but, actually, each pin is carried several inches downward before being sundered, as shown in Fig. 8. It makes little difference whether a new or a worn disc is used, i.e. whether a thin (0·01 in. or less) or a thick (0·05 in.) skull is left in the container, the essential features remain as shown in Fig. 8, with relatively unimportant changes in detail. With composite billets, the skull also is composite, the junctions between different layers of brass appearing at their expected places with a slope conforming to that of the pins.

The top portion of the skull (for a length of about 0·75 in.), formed from the upper edge of the billet, consists of distorted, vertically-elongated as-cast grains, indicating that it does not reach recrystallization temperature during or after distortion, presumably because of the cooling effect of disc and container in this region. With one exception, all other parts of the skull, including pins, consist of small, approximately equi-axial grains, the exception being the outside of the skull of 60 : 40 brass billets, which shows the as-cast structure distorted with a downward curvature corresponding with that of the pins. The remainder of a 60 : 40 brass skull consists of fine-grained alpha and beta constituents.

Skulls as removed from the container are not soft, but are noticeably springy. Hardness measurements reveal the following values : 118–140 Vickers D.P.N. for 60 : 40 brass, and 117–175 D.P.N. for 76 : 22 : 2

brass. The highest value is at the top, where distorted as-cast grains are present, and hardness above average is also found at the bottom, where some stretching occurs when skull and discard are torn apart during their removal from the container. Apparently, recrystallization of the skull is started by the hot-working shearing action of the bottom outer edge of the disc, and hardening follows through the passage of the outer face or side of the disc over the chilled skull.

In seeking for an explanation of the way in which the pins are turned downwards for several inches in the skull before being thinned to breaking point, the following possibilities have to be considered :

(1) That the skull is formed by back extrusion of the brass into the narrow annulus between disc and container. This is not a likely explanation, as a skull is rarely more than 1 in. longer than the billet from which it is obtained, and most, if not all, of this increase in length can be accounted for by stretch at the bottom during ejection of the discard from the container and by the forcing of the upper edge of the billet up the sloping face of the disc during upsetting in the first stage of extrusion.

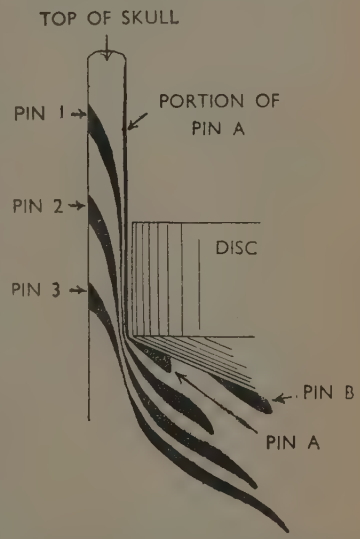

FIG. 9.—Diagrammatic Vertical Section Through Corner of Partly Extruded Brass Billet Suggesting How the Disc Bends Down the Pins in the Skull. Thickness of skull has been exaggerated.

(2) That, in view of the manner in which the pins are carried down and into the body of the billet (Figs. 4, 5, and 7), it is to be expected that they would be carried down and in ahead of the disc. This is certainly a cause, but it does not explain why pin 1 is generally carried down the skull a slightly greater distance than the other pins, despite the fact that relatively little extrusion of the billet has occurred by the time the disc reaches the level of pin 1.

(3) A considerable proportion of the elongation of the pins in the skull appears to be caused by the disc pushing ahead of itself a cushion or corner of brass which prevents a clean shearing of the pins. Evi-

dently, this cushion bends the pins down and elongates them to breaking point. Support for this explanation is found in the fact that part of the outermost top pin *A* (Fig. 2) is often to be found as a streak down the inside of the skull, sometimes for the full length, as indicated in Fig. 9.

In one experiment, 26 pins were inserted in a line down the side of a billet. In a vertical (i.e. longitudinal) section of the skull made from this billet, from seven to ten pins could be seen at any traverse across the skull below the level of the head of pin 10, i.e. pins 1 to 9 were carried down beyond the head of pin 10, as shown in Fig. 13 (Plate XIII). Pin 1 petered out on the inner wall at the level of pin 11. In the short length of skull shown in Fig. 13 the pins appear to be parallel to the walls, but actually they commence farther up at the outer wall (left) and gradually thin out and vanish at the inner wall (right).

The thinnest brass skull cut in any experiment was 0·005–0·01 in. thick. It is probable that, if a billet could be extruded in a non-lubricated container with a close-fitting disc so that no skull was left in the container, the as-cast surface of the billet would be drawn inwards, like the pins in Fig. 4, as if it were composed of an almost infinite number of minute pins. At the completion of extrusion, the outer top edge of the discard should then consist entirely of a rim of minute pin ends, representing the residue of the as-cast surface.

VI.—Flow of Copper in a Non-Lubricated Container.

Under the conditions so far described, the normal type of flow for copper is different from that for brass and is as shown in Fig. 10 (upper). The diagonal type of flow is replaced by flow from the bottom of the billet across the face of the die. Each pin in turn disappears into the shell, and in no cross-section of a shell are all five pins to be seen together. In a billet three-quarters extruded, as in Fig. 10 (upper), pin 3 is usually present close to the face of the die but so attenuated that, in some instances, it can be seen only with the aid of a lens.

The skull of deoxidized arsenical and non-arsenical copper is thin, clean, and polished on inner and outer walls, and without the five pin heads down the outer wall. That of oxygen-bearing copper is similar except for some adherent oxide on the outer wall and, at times, a slightly tarnished inside wall. Typically, only one pin (apparently pin 1) is to be seen, either as a flat streak down the outside of the lower part of the skull, or just inside the skull running parallel with the walls, and part of top pin *A* is usually to be seen distributed as a flat

streak down the inside of the skull, as shown in Fig. 11. Hardness values of 64–95 Vickers D.P.N. were obtained on skulls of deoxidized copper.

This difference in flow between brass and copper does not appear to be due to the higher extrusion temperature of copper, as brass and copper billets can be placed in the preheating furnace together and, in

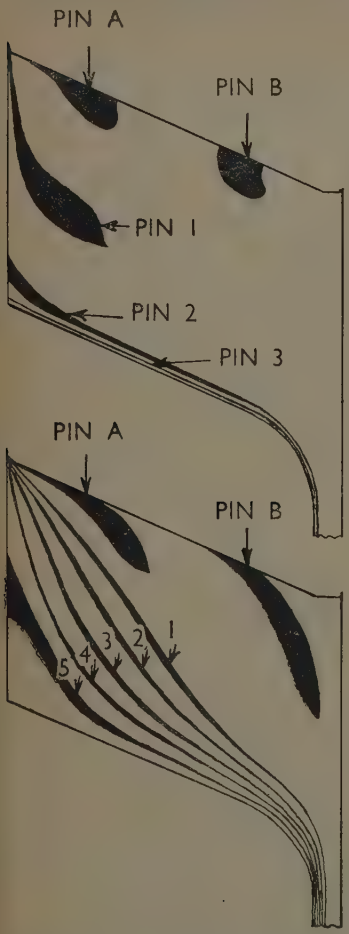

Fig. 10.—Vertical Sections Through Copper Billets Three-Quarters Extruded in a Non-Lubricated Container. (*Upper*) illustrates type of flow for a billet with an oxidized surface. (*Lower*) illustrates type of flow for a billet protected from oxidation.

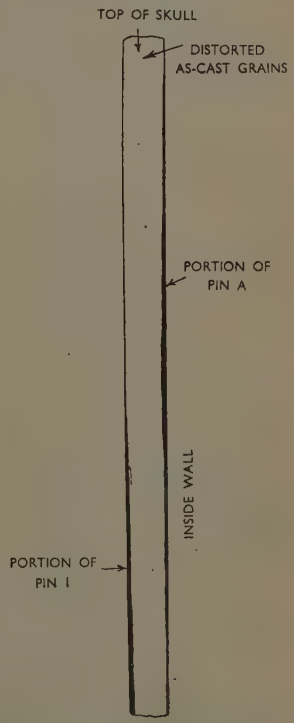

Fig. 11.—Vertical Section Through Skull of a Copper Billet Extruded in a Non-Lubricated Container. Thickness is drawn on a scale twenty times that of length.

the press, brass will flow in the manner shown in Fig. 4 and copper in the manner shown in Fig. 10 (upper). The reason becomes apparent when one examines the inside of the container and the surfaces of the skulls when a press is running on copper.

It is well known to press operators that oxidation of copper billets should be avoided as much as possible by controlling the atmosphere in the pre-heating furnace. But as this is difficult to achieve with the usual type of furnace, some degree of oxidation occurs. Yet, although copper billets enter the container with an oxide envelope, the inner and outer surfaces of the skulls, as already mentioned, are free from oxide. This is to be expected for the inner surface, which is sheared by the disc, but it is scarcely to be expected for the outside. The explanation is that the oxide envelope is held by the container while the copper slips down within the envelope and passes across the die. The oxide accumulates on the container wall like a layer of blue-black enamel and periodically flakes off in patches between extrusions and drops below or to the front of the press. The lower or sloping face of the disc becomes highly polished with adherent oxide, and some oxide is likely to be carried down on the shells. Frequent lubrication of the die prevents the adherence of oxide to its working surface. The presence of oxide on the container reduces the clearance between disc and container and accounts for the comparative thinness of copper skulls. The thinnest copper skull made in any experiment was 0·005–0·01 in. thick.

If this explanation is valid, one would expect that, if a copper billet could be prevented from oxidizing, it should flow like brass, and that, if a copper envelope could be fixed to a brass billet, the brass should flow like copper. Both expectations can be realized by electrodepositing a layer of chromium on a copper billet and a layer of copper on a brass billet. Only a thin layer of chromium is needed, but the copper layer must be thick to allow for the thick oxide envelope formed in pre-heating. The oxidation of the chromium to a layer of chromic oxide effectually holds the skin of the copper billet against the container wall and causes the billet to flow in the manner shown in Figs. 4 and 10 (lower), while the oxidation of the copper on the brass causes the brass billet to flow according to the manner shown in Fig. 10 (upper), leaving a skull composed of copper on the outside and brass on the inside. A similar, but not so consistent, result can be obtained by coating a copper billet with a protective paste of sodium silicate and red ochre before pre-heating, and by turning off the peripheral region of a brass billet and replacing it with a tight-fitting copper tube.

An intermediate type of flow can be obtained with copper by plating the lower one-quarter or one-half with chromium to check the flow of

metal across the die face. The plating is less effective when applied to the upper portion only of a billet.

The type of flow shown in Fig. 10 (upper) is to be seen not only when a press is running continuously on copper, i.e. when the container is likely to be well lined with oxide, but also when an oxidized copper billet is extruded singly during the extrusion of brass. The necessary condition seems to be an oxide envelope on the billet rather than an oxide lining on the container.

The size of the shell has but little effect on the type of flow; for example, a discard made from a billet 6·2 in. dia. extruded to a shell 4 in. external dia. × 3·3 in. internal dia. shows the same general features as one made from a billet of the same diameter extruded to a shell 2·36 in. external dia. × 1·97 in. internal dia. (60 × 50 mm.).

It is well known that a container which is lined with copper oxide can be cleaned by extruding one or two brass billets during a run on copper. In these circumstances, the copper oxide on the container has no influence on the type of flow exhibited by the brass; it merely adheres to the outside of the brass and is removed with the brass skull. If the copper oxide lining on the container is thick, it may be drawn into the brass skull at places, like the pins shown in Fig. 8, but on a microscopic scale, as shown in Fig. 14 (Plate XIII).

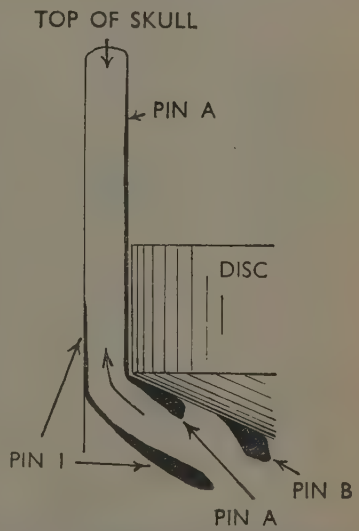

Fig. 18.—Diagrammatic Representation of Manner in Which a Skull is Formed from a Copper Billet Extruded in a Non-Lubricated Container. The thickness of the skull has been exaggerated.

A characteristic feature of a copper skull is a banded structure parallel to the walls, especially towards the bottom portion of the skull, as shown in Fig. 15 (Plate XIV). A copper skull does not represent a full-length outer layer of the billet as does a brass skull formed in a non-lubricated container. There is a probability that a copper skull is formed largely by back extrusion of the upper outer portion of the billet, as shown in Fig. 18.

VII.—Experiments with Turned Brass Billets.

It is worth recording that, in the pre-heating furnace, aluminium-brass (76 : 22 : 2) billets having an as-cast skin are brighter, i.e. appear to be hotter, than those that have had the as-cast skin removed by turning. Hence arises the erroneous opinion among press operators that turned billets of this alloy can be successfully extruded at a lower temperature than unturned billets. To test the possibility that the absence of an as-cast skin might affect the nature of flow, several turned aluminium-brass billets were prepared with the usual pins and extruded in a non-lubricated container, alternately with unturned billets of similar composition. The usual sections through skulls, discards, and shells proved that the type of flow was the same for all billets and conformed to that for brass as shown in Fig. 4.

There is no reason to suppose that turning a copper billet would have any influence on the mode of flow.

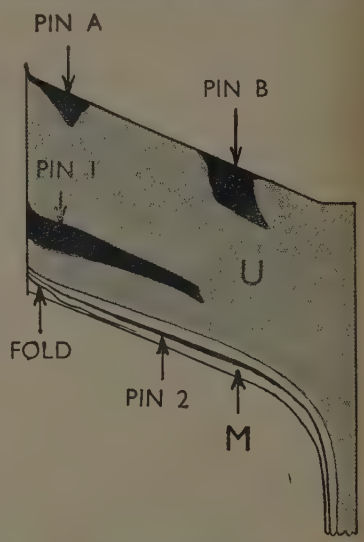

Fig. 19.—Vertical Section Through Composite Brass Billet Three-Quarters Extruded in a Lubricated Container.

VIII.—Flow of Brass in a Lubricated Container.

When lubricant is placed on the container wall as well as on the die, mandrel, and side of disc, the flow of brass resembles that of copper as just described for a non-lubricated container. A typical example for composite brass billets is shown in Fig. 19, for comparison with the flow shown in Fig. 7.

The skull is usually thin and comparatively short and may be absent when or where lubricant has been applied liberally to the container. As with a copper skull, the pin heads are not present on the outer wall, nor are the pins to be seen in vertical sections turned downwards one below the other as shown in Fig. 8. A portion of a pin, probably pin 1, is usually present as a streak at the lower end of the outer wall, or just inside the wall, and a portion of top pin *A* is usually

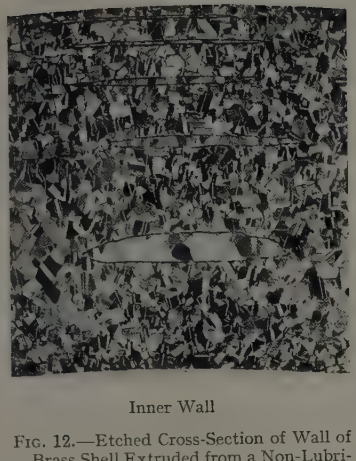

FIG. 12.—Etched Cross-Section of Wall of Brass Shell Extruded from a Non-Lubricated Container, Showing Positions of Side Pins 1 to 5. Pin 1 (the largest) is near the inner wall and pin 5 is close to the outer wall. The billet has been three-quarters extruded. × 11.

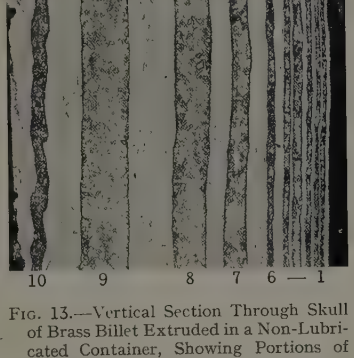

FIG. 13.—Vertical Section Through Skull of Brass Billet Extruded in a Non-Lubricated Container, Showing Portions of Ten Pins. Pin 1 is at the extreme right, close to the inner wall, and part of the head of pin 10 is at the extreme left near the outer wall. Thickness of skull was 0·03 in. × 60.

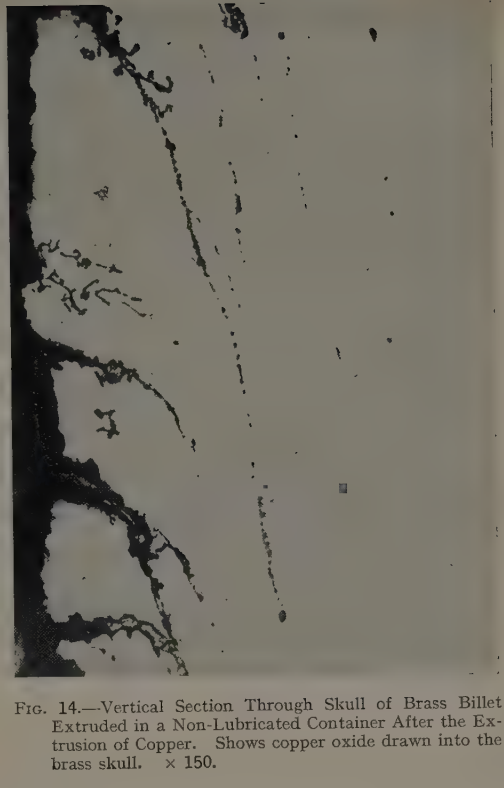

FIG. 14.—Vertical Section Through Skull of Brass Billet Extruded in a Non-Lubricated Container After the Extrusion of Copper. Shows copper oxide drawn into the brass skull. × 150.

[*To face p.* 178.

FIG. 15.—Vertical Section Through Skull of a Copper Billet Extruded in a Non-Lubricated Container. Shows only one pin (side pin 1) running parallel to the walls and a strongly banded structure also parallel to the walls. The skull was 0·03 in. thick. × 100.

FIG. 16.—Vertical Section Through Partly Extruded Discard from Brass Billet Extruded in a Non-Lubricated Container, Showing how Charcoal Inclusions and Brass Sealing Pins are Drawn into the Billet. Half natural size.

FIG. 17.—Same as Fig. 16 except that the Billet was Partly Extruded in a Lubricated Container. Shows how charcoal inclusions and brass sealing pins pass one after the other across the die instead of being drawn into the billet. Half natural size.

present as a streak down the inner wall. A pin head is sometimes to be seen on the under-face of the discard where it was in contact with the die. The banded structure described for copper skulls is also a feature of brass skulls produced in a lubricated container.

The skull corresponding to the discard shown in Fig. 19 was not divided into *U*, *M*, and *L* portions, but consisted largely of *U* portion with a small proportion of *M* towards the bottom. In an experiment where *U* and *L* consisted of 70 : 30 brass and *M* of aluminium brass (76 : 22 : 2), the upper part of the skull consisted of 70 : 30 brass, the middle portion contained 0·04% aluminium, and the bottom portion contained 0·2% aluminium. This is a small proportion for a billet that contained 2% in the middle half.

When a container is unevenly lubricated, the flow at the driest places may be of a half-and-half type, that is to say, neither similar to the flow shown in Fig. 4 nor to that shown in Fig. 10 (upper), but a blend of the two.

In general, it may be said that so distinct are the features of skulls made from billets extruded in different ways that they may be relied on to indicate the nature of flow without resort to sections through discards and skulls.

IX.—Flow of Copper in a Lubricated Container.

Copper flows in the same way in a lubricated as in a non-lubricated container, but the skulls formed in a lubricated container are likely to be short and the discards are likely to have a loose ring or rim of metal on the lower outer edge where some flowing metal collects at corner *Y*. When excess lubricant is used, the outer portion of the billet may cut in across *Y* to produce a double (blistered) wall on the shell.

It may be asked why a long skull is left when copper is extruded in a non-lubricated container. The answer seems to be that there is sufficient resistance in separating the outside of the billet from its oxide envelope to allow the disc to squeeze or back-extrude a thin cylinder of metal into the annulus between disc and container.

X.—Dry *v.* Lubricated Container.

The practical advantage of not lubricating the container for brass is that, as the skin of the billet is left in the container, there is no need to ensure that the as-cast billets have smooth surfaces; but that there is a limit to the degree of surface imperfection permissible is clearly indicated by the fate of the pins. In one experiment, pieces of charcoal were placed in the drill holes and sealed in with short brass pins to

simulate sub-surface inclusions. They were drawn into the body of the billet and into the shell like plain pins (Fig. 16, Plate XIV) but with the difference that they appeared on the outside of the shell as an elongated broken blister. In another experiment, the drill holes were left unfilled. They appeared as fine threads in vertical sections of the skull and discard and in sections of the shell.

In the flow obtained with brass in a lubricated container and with copper in either a lubricated or a non-lubricated container, defects on the outside of a billet are likely to appear on the outside of a shell rather than between the walls. In one experiment, charcoal was placed in the drill holes and covered with brass pins as described above for a non-lubricated container. Instead of being drawn into the body of the billet during extrusion, the inclusions passed in turn over the face of the die (Fig. 17, Plate XIV), to appear immediately as a line of dirty broken blisters. In Fig. 17, pins 1, 2, and 3 are present, but 4 and 5 have passed into the shell.

While the lubricated type of flow is easier on the press than the non-lubricated type, in the sense that, by throttling the valve, lower pressures can be employed, there is a likelihood, as already mentioned, that the peripheral portion of the billet will fold in across corner *Y* to produce a double, blistered wall on the shell and a corner rim of loose metal on the discard. A similar defect is likely to arise on the inner wall of a shell towards the end of extrusion if lubricant is applied liberally to the lower or sloping face of the disc. In this case, the top skin of the billet folds in across corner *X*, leaving the discard with a clean surface against the disc. In a billet three-quarters extruded with a lubricated disc, pin *B* is to be seen not in the position and with the shape shown in Figs. 4, 5, and 7 on the one hand, or Fig. 10 (upper) on the other hand, but vertically elongated close to and parallel with the mandrel.

XI.—The Structure of the Plug.

The structure of the plug pushed out by the mandrel (Fig. 1(*b*)) has been studied by means of composite billets of the type shown in Fig. 6, for both copper and brass, and by means of pins 0·5 in. dia. inserted axially to within 1 in. of the bottom (Fig. 20). In some experiments, the upper half of the pin was composed of brass (or copper, as the case might be) of slightly different composition to the lower half to facilitate comparison after etching.

A typical plug made in the 1000-ton press from a composite billet, using a square-ended mandrel, is shown in Fig. 21 (left), and a typical plug made in the 600-ton press, using a pointed mandrel, is shown in

Fig. 21 (right). The experiments demonstrated that a square-ended mandrel spreads the axial pin into arrow-head shape, while a pointed mandrel pierces the upper part of the pin, causing some of it to be left in the billet and, ultimately, on the inner wall of the shell. They

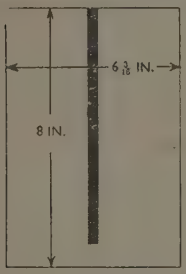

FIG. 20.—Method of Inserting Pin Axially in Billet.

FIG. 21.—(*Left*) Showing How Axial Pin is Transferred to Plug by a Square-Ended Mandrel. (*Right*) Showing How Axial Pin is Pierced and Only Partly Transferred to Plug by a Pointed Mandrel.

further showed that, with both square-ended and pointed mandrels, the greater part of the plug is composed of the lower part *L* of the billet (Fig. 22); that, with square-ended mandrels, the middle *M* and upper *U* portions of the billet are also represented in the plug, while, with pointed mandrels, the upper portion *U* is not represented; and that the full length of the axial region of a billet, at least up to a diameter of 0·5 in., is transferred to the plug by a square-ended mandrel, but not with a pointed mandrel.

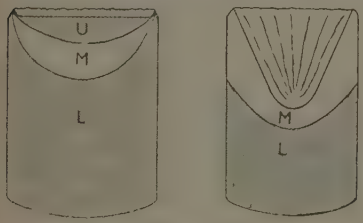

FIG. 22.—Vertical Sections Through Plugs Made from Composite Billets. (*Left*) plug made in 1000-ton press with a square-ended mandrel. (*Right*) plug made in 600-ton press with a pointed mandrel.

From a practical aspect, the experiments indicated that axial porosity in a billet, when not widespread, should be wholly pushed into the plug by a square-ended mandrel, whereas with a pointed mandrel part of the porosity should appear as spill and scale on the inner wall of the shell. When axial porosity extends beyond the truly axial region, even square-ended mandrels are not likely to mask its effects, as some of it will trail out from the tips of the arrow-head shown in Fig. 21 (left), to appear as spill and scale on the inner wall of the shell.

XII.—Correlation Between Type of Flow and Structure of Shell.

By means of etched cross-sections of shells made from composite billets, it is possible to relate the different parts of a billet with different parts of the shell for both principal types of flow, as shown in Fig. 23. Because of the great length of the shell compared with that of the billet, it is impracticable to give a true scale representation of billet and shell; hence, in Fig. 23 the length of the shell is greatly shortened and the thickness exaggerated, while the discard is also drawn out of proportion; the drawing is therefore diagrammatic.

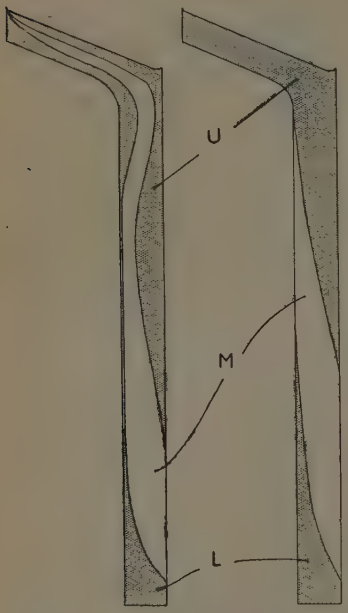

Fig. 23.—Diagrammatic Vertical Sections Through One Side of Shells and Discards of Composite Billets Extruded in Non-Lubricated Container (*left*) and Lubricated Container (*right*). Thickness of shells and discards has been greatly exaggerated in proportion to length of shell.

It will be seen that, in spite of the different ways in which billets flow in the press, the structure of the shell is basically similar for all types of flow to the extent that there are long sloping surfaces separating the *U*, *M*, and *L* portions. In a shell made from an as-cast (i.e. non-composite) billet there would, of course, be no dividing interfaces, such as are shown in Fig. 23, but the distribution in the shell of successive horizontal elements of the billet would conform to this pattern.

In all cases, whatever may be the degree of friction between billet and container, the mandrel and disc play an important part in forcing or carrying down the inner portions of the billet.

The essential difference between what may be broadly termed non-lubricated and lubricated types of flow is that in the former the outer wall of the shell is wholly composed of the bottom part of the billet and the inner wall largely composed of the upper part of the billet, while in

the latter the bottom and top of the billet more nearly correspond with the lower and upper parts of the shell. The controlling factor appears to be the degree to which the outside of the billet adheres during extrusion to the container wall, or, what amounts to the same thing, to an oxide layer introduced into the container by the billet.

There are, however, important differences between oxide layers, from the thin zinc oxide on brass to the thick scale on copper–nickel. With phosphorus-deoxidized arsenical and non-arsenical coppers, both of which form a scale that flakes on cooling, the billet appears to be able to slip or slide within its oxide envelope and thereby obtain the advantage of lubrication under pressure in extrusion. Oxygen-bearing (H.C.) copper, which has a scale that is largely adherent at room temperature, flows like deoxidized copper, while 70 : 30 copper–nickel, which has a thick adherent scale at room temperature, flows like brass. It is possible that the explanation for these differences in behaviour lies in the degree to which metal and oxide can slide one past the other under pressure at elevated temperature.

XIII.—Conclusions.

In presses of the kind used in the experiments, the type of flow exhibited by copper and copper alloys is determined by the friction between the skin of the billet and the press container. Other factors are of minor importance.

Flow is of two types, depending on whether or not the skin of the billet remains in place against the container wall. In a dry or non-lubricated container, brass and copper–nickel billets flow diagonally to the die orifice, and peripheral portions of the billet are drawn into the body of the billet and carried down between the walls of the hollow or shell. In a lubricated container, this diagonal type of flow is replaced by flow from the bottom of the billet across the die, and peripheral portions of the billet are not drawn into the body of the billet to nearly the same extent as with the former type.

Normally, phosphorus-deoxidized arsenical and non-arsenical coppers and oxygen-bearing (H.C.) copper exhibit the second type of flow, but only because they carry into the container an oxide envelope which functions as a lubricant for the underlying metal. Hence, lubrication of the container does not affect the type of flow for copper; however, when copper is prevented from oxidizing in the pre-heating furnace it flows like brass and copper–nickel in a dry or non-lubricated container. When a layer of copper is placed on a brass billet and allowed to oxidize in the pre-heating furnace, the brass flows like copper.

The presence of a thick copper-rich oxide layer on a billet, *per se*, is not a guarantee that the billet will flow as if the container were lubricated, as witness the non-lubricated type of flow shown by copper–nickel; the controlling factor with the oxide layer appears to be the degree to which the billet can slip or slide within its oxide envelope under pressure in the container. A further study of this feature might yield results of value in the hot drawing of metals.

The structure of the skull left in the container at the end of extrusion indicates the manner in which the billet has flowed during extrusion.

Despite the radically different ways in which a billet can be made to flow by controlling the degree to which it adheres to the container wall, there is a good deal of similarity in the structure of the extruded shells. In what may be termed the non-lubricated type of flow, the whole of the outer wall of the shell is made from the bottom portion of the billet, and the greater part of the inner wall is made from the upper portion of the billet. In the lubricated type of flow the lower and upper portions of the shell (i.e. the first and last portions to be extruded) more nearly correspond with the lower and upper parts of the billet.

From a practical point of view, the principal distinction between the two types of flow is that superficial defects on the billet are likely to appear between the walls of the shell with the non-lubricated type and on the outer surface of the shell with the lubricated type, and double or blistered walls are likely to arise with the lubricated type.

A scaly inner wall on the shell, due to axial porosity in the billet, is more likely to arise from the use of a pointed mandrel than a blunt or square-ended mandrel.

ACKNOWLEDGEMENTS.

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THE RECOVERY AND RECRYSTALLIZATION OF ROLLED ALUMINIUM OF COMMERCIAL PURITY.*

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(Contribution from the Research Laboratories of the British Aluminium Co., Ltd.)

Synopsis.

A study was made, by means of ultimate tensile strength determinations, of the process of recovery and recrystallization of polycrystalline aluminium sheet of normal commercial purity within the temperature range 200°–325° C. The isothermal annealing curves, in which ultimate tensile strength is plotted against the logarithm of the time, are continuous curves exhibiting no discontinuity corresponding to the onset of recrystallization. The evidence of X-ray diffraction patterns shows that recrystallization commenced at a level of 7½ tons/in.² for all samples of hard-rolled aluminium examined.

The activation energy of the process, which appears to be independent of process variables, is 51,240 cal./g. atom.

It is suggested that the observations are consistent with the theory that both recovery and recrystallization take place by the diffusion of dislocations in the lattice and the mutual annihilation of those of opposite sign.

I.—Introduction.

The subject of recovery and recrystallization of cold-worked metals has attracted a good deal of attention during the last decade or so and many papers have been published bearing on the matter. An excellent summary and bibliography of these is given by W. G. Burgers.[1] When a cold-worked metal is heated, the first observable effect is usually a gradual return of its mechanical and other properties towards the values for the annealed metal. If the temperature is low, so that visible recrystallization does not take place, then the metal may reach a steady state such that the properties do not change over a long period of time. Thus Kornfeld,[2] working with single crystals of aluminium, found that at temperatures of 150°–250° C. the yield point fell to an approximately steady value in about 30 min., this value being lower the higher the temperature. On the other hand, Cook and Richards,[3] working with copper, found no change in hardness until, after a definite incubation period, recrystallization set in, when the hardness decreased proportionately to the degree of recrystallization. An incubation period

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before the appearance of visible recrystallization was found by Anderson and Mehl,[4] working with lightly deformed aluminium, but these workers did not determine the changes in mechanical properties.

In the experiments to be described in the present paper, an attempt has been made, using polycrystalline aluminium of normal commercial purity, to bridge the gap between recovery and recrystallization and to determine whether they are in fact two distinct processes, each with its own activation energy, or whether they are merely different stages of a single process with but a single activation energy.

To this end, the isothermal annealing curves for various samples of aluminium sheet have been determined over a wide range of temperatures, and it has been shown that there is no obvious discontinuity between recovery and recrystallization, other than the appearance of new crystals, and that both processes have the same activation energy, within experimental error.

It was known that certain treatments could have a marked effect on the recrystallization temperature of aluminium. Accordingly, the effect of such process variables was studied, and it has been shown that although the rate of softening may be changed by a factor of ten or more, the activation energy remains unaltered.

II.—Material Used.

The metal used for the greater part of these experiments was 0·036-in. strip-rolled aluminium of four different compositions :

	Si, %.	Fe, %.
A	0·15	0·35
B	0·15	0·45
C	0·25	0·35
D	0·25	0·45

Both chill- and continuously-cast metal were available in each composition. Half the metal had been rolled to 0·036 in. without any process anneal, while the other half had been annealed at 0·144 in. thickness, so that in its final state it had received 75% cold reduction.

Certain other metal samples were used for some of the experiments. Details of these are given in the appropriate sections of the paper.

III.—Experimental.

Annealing was carried out either in an electrically heated muffle with forced-air circulation or in a salt bath, depending on the expected rate of softening. Where this was slow, and long annealing times were involved, the muffle was used ; this gave a rate of heating of about 1½ hr.

to 250° C. Where softening was rapid, and the annealing times were correspondingly short, a small gas-heated salt bath was used which gave a rate of heating of about 20 sec. to 250° C.

Temperature control for the muffle was by means of a potentiometric controller using a Chromel–Alumel couple. The charge temperature was determined by means of one or more similar couples inserted in holes drilled in a small block of aluminium. This constituted, in itself, a dummy charge and was placed centrally on the furnace among the bundles of specimens. The temperature was controlled to about $\pm$ 1° C. and determined to about $\pm$ 2° C.

For the salt bath, temperature control was manual, but the use of a governor so reduced the pressure variations of the gas mains that drift was very slow and the temperature could readily be held to $\pm$ 2° C. Temperature was determined by means of a Chromel–Alumel couple in an iron sheath dipping into the molten salt. The accuracy of determination was probably about $\pm$ 2° C.

Annealing times were measured from the moment at which the metal reached the desired temperature : for muffle anneals this was taken as being the moment at which the couples in the dummy charge indicated this temperature, while for salt-bath anneals it was taken as 20 sec. after immersion. This 20-sec. heating interval was determined by means of an experiment with a dummy specimen, having an inserted thermocouple, and using a quick-reading galvanometer.

Throughout the investigation, standard ½-in.-wide tensile test-pieces were used as specimens, the dimensions being those given in British Standard Specification 18 : 1938 for test-piece *A* (column (i)). These were cut transversely to the direction of rolling. Specimens were tied together in bundles of as many as 50–60 for the muffle anneals, but in the salt bath not more than one, or at the most two, specimens were annealed at the same time.

The changes taking place during annealing were followed by determination of the ultimate tensile strength. This determination was in all cases carried out on duplicate specimens. In certain cases, X-ray diffraction patterns were also obtained, using the transmission method with a molybdenum target. These patterns were examined to determine the degree of recrystallization, which was assessed on an arbitrary scale, 0 corresponding to metal with no trace of new crystals and 5 to metal in the completely recrystallized state.

1. *Influence of Composition.*

In the initial experiments, samples of all four compositions, in both methods of casting and both with and without a process anneal, were

annealed for times varying from 15 min. to 1000 hr. at temperatures of 200°, 220°, 240°, and 260° C.

The mean figures for chill- and continuously-cast metal annealed at 260° C. are grouped according to composition in Tables I and II,

TABLE I.—*Effect of Composition on Rate of Softening (no Process Anneal).*

Time at 260° C., hr.	Ultimate Tensile Strength, tons/in.²			
	A.	*B.*	*C.*	*D.*
0	12·15	12·48	12·38	12·33
½	9·34	9·92	9·79	9·61
1	8·68	9·41	9·53	9·22
2	8·07	8·96	8·95	8·86
3	7·64	8·31	8·29	8·23
8	6·99	7·29	7·57	7·50
24	5·86	5·98	6·49	6·05

TABLE II.—*Effect of Composition on Rate of Softening (with Process Anneal).*

Time at 260° C., hr.	Ultimate Tensile Strength, tons/in.²			
	A.	*B.*	*C.*	*D.*
0	10·59	10·81	10·55	10·91
½	7·64	7·78	7·82	7·75
1	7·24	7·25	7·66	7·24
2	6·93	6·82	7·10	6·89
3	6·04	6·13	6·42	6·21
8	4·97	5·22	5·12	5·37
24	4·73	5·01	4·84	5·09

Table I being for metal with no process anneal and Table II being for metal process-annealed at 0·144 in. There is an obvious difference produced by the process anneal which will be discussed in detail later, but in neither Table is there any indication that one composition softens at a different rate from another. There are small differences, it is true, in the actual figures, but these are all explicable by the experimental errors of tensile testing or by differences in the initial tensile strengths, due largely, if not entirely, to chance variations in the rolling procedure.

2. *Influence of Casting Method.*

In Table III the mean figures for all compositions have been grouped according to the method of casting, either chill or continuous. There is an initial difference of about ½ ton/in.² in favour of the continuously cast

metal, but this disappears as softening proceeds and is also completely removed by a process anneal. It seems probable that this

TABLE III.—*Effect of Casting Method on Rate of Softening.*

Time at 260° C., hr.	Ultimate Tensile Strength, tons/in.²			
	No Process Anneal.		Process Annealed.	
	Continuous Casting.	Chill Casting.	Continuous Casting.	Chill Casting.
0	12·42	12·06	10·77	10·62
½	9·85	9·32	7·53	7·82
1	9·35	8·92	7·26	7·39
2	8·78	8·60	6·87	6·94
3	8·13	8·10	6·15	6·29
8	7·33	7·36	5·14	5·23
24	6·09	6·11	4·89	4·97

difference is a constitutional one, due, it is believed, to a greater proportion of the silicon being retained in solid solution by the more rapid chilling of the continuous-casting process.

3. *Form of the Annealing Curves.*

Having shown that neither variations in composition within the limits studied, nor differences in the method of casting, have any influence on the rate of softening, it is legitimate to ignore these variables in plotting tensile strength against time. This has been done for four different temperatures in Fig. 1 for metal which has had no process anneal and in Fig. 2 for the same metal process-annealed at 0·144 in. For both practical and theoretical reasons it has been convenient to plot tensile strength against the logarithm of the time.

The curves for the various temperatures are similar and, within experimental error, are superposable by displacement along the time axis. The curves for metal with and without a process anneal are also superposable by displacement along the ultimate tensile strength axis. This is shown in Fig. 3, where both sets of figures have been plotted after adding 1·9 tons/in.² to the figures for the metal process-annealed at 0·144 in. This figure is not the same as the difference between the mean tensile strengths before annealing, which works out at 1·56 tons/in.² The discrepancy must be due to a lesser degree of strain relief with the process-annealed metal during heating to the annealing temperature.

Except that the curve for 240° C. is slightly out of place, owing presumably to a small error in temperature control, the curves are

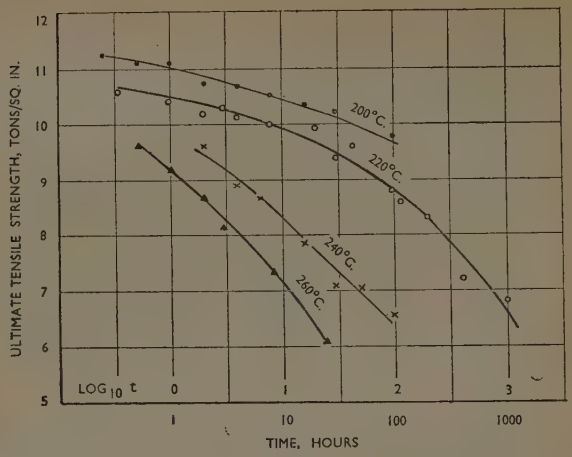

FIG. 1.—Isothermal Annealing Curves. No process anneal.

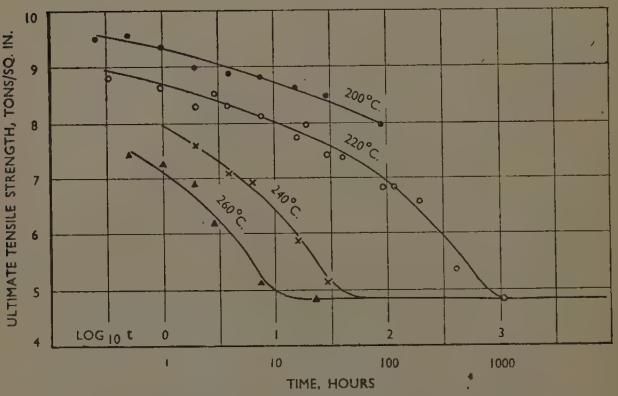

FIG. 2.—Isothermal Annealing Curves. Metal process annealed.

evenly spaced along the logarithmic-time axis. This is confirmed by Fig. 4, where the logarithm of the time to reach a tensile strength of 7 tons/in.^{2} is plotted against the reciprocal of the absolute temperature. The times have been read off the curves in Figs. 1 and 2, extrapolated in the case of the 200° C. curves. The points fall reasonably well on two parallel straight lines, confirming, as was suggested by Fig. 3, that, although softening is more rapid for metal which has been process-annealed, the temperature coefficient of the process is the same.

The slope of these lines is a measure of the activation energy of the

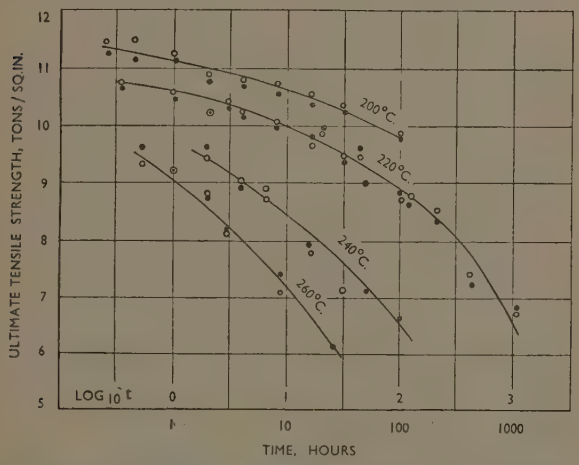

Fig. 3.—Superposed Isothermal Annealing Curves from Figs. 1 and 2.

● No process anneal.
○ Process annealed + 1·9 tons/in.^{2}

process, and it was therefore of interest to determine this more accurately and also to see whether it was a constant for the metal or whether it varied from one sample to another according to previous history. A more detailed study was therefore made of the softening behaviour of eight different samples of aluminium sheet. Details of these are given in Table IV. The temperatures employed were 220° C. and either 300° or 325° C., isothermal annealing curves being plotted for each sample. From these curves the slope of the log t–$1/T$ line was calculated for various tensile strengths. The figures obtained are given in Table V.

Examination of these figures shows, firstly, that although the slope appears to be steeper for some samples than for others, there is no treat-

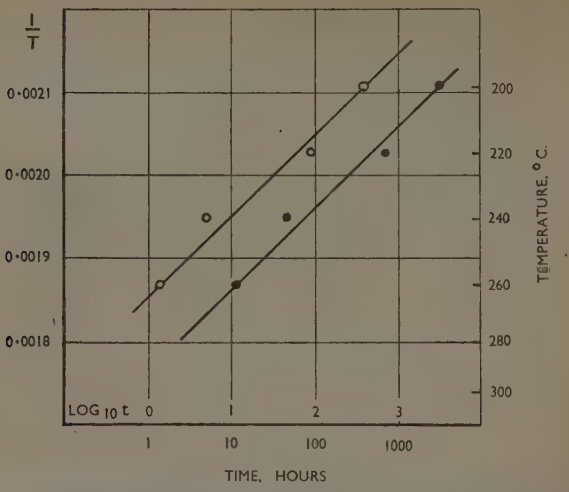

FIG. 4.—Relation Between Times of Softening to 7 tons/in.^{2} Ultimate Tensile Strength and Reciprocal of Absolute Temperature.

● No process anneal.
○ Process annealed.

TABLE IV.—*Metal Used for Experiments on Effect of Process Variables.*

Identity.	Method of Casting.	Cold Work, % reduction.	Hot-Working Temperature, ° C.	Soaking Time, hr.
1	Chill	Hard	520°	4
2	,,	75	520°	4
3	,,	20	520°	4
7	,,	28	520°	4
*A*1	Continuous	Hard	425°	47
*A*2	,,	82	425°	47
*A*8	,,	82	500°	9
*A*16	,,	Hard	525°	4
*A*20	,,	,,	420°	13
*A*24	,,	,,	515°	13
*B*1	,,	,,	510°	4

All except *A*24 and *B*1 were 99·2% purity. *A*24 was 99·5% purity and *B*1 was 99·8% purity.

ment which can be said to have a specific effect, and it seems probable that such differences are really due to experimental error. Statistical analysis cannot be easily applied, since the various figures for each sample, being taken from the plotted curves, are not really independent estimates of the slope.

It was also of interest to determine whether there was any tendency for the slope to vary consistently with the level of ultimate tensile

TABLE V.—*Determination of Slope of log t–1/T Line.*

Identity.	Temperature Range, ° C.	Ultimate Tensile Strength Level, tons/in.²	Slope.
1	220°–325°	9	$1{\cdot}15 \cdot 10^4$
	,,	8½	1·18
	,,	8	1·15
	,,	7½	1·13
	,,	7	1·10
2	220°–325°	8	1·07
	,,	7½	1·07
	,,	7	1·11
	,,	6½	1·13
	,,	6	1·14
3	280°–325°	5½	1·17
7	280°–325°	5½	1·16
*A*1	220°–300°	7	1·17
	,,	6½	1·11
	,,	6	1·10
*A*2	220°–300°	7	1·17
	,,	6½	1·14
	,,	6	1·17
	,,	5½	1·11
*A*8	220°–300°	8	1·11
	,,	7½	1·06
	,,	7	1·06
	,,	6½	1·06
	,,	6	1·08
	,,	5½	1·06
*A*16	220°–300°	7½	1·24
	,,	7	1·20
	,,	6½	1·17
	,,	6	1·14
*A*20	220°–300°	7½	1·11
	,,	7	1·09
	,,	6½	1·06
	,,	6	1·04
*A*24	220°–300°	7½	1·10
	,,	7	1·12
	,,	6½	1·12
	,,	6	1·11
	,,	5½	1·07
*B*1	250°–300°	6½	1·00
	,,	6	1·10
	,,	5½	1·19

strength at which it was determined. Any such variation might be taken as indicating a change in the softening process from recovery to recrystallization.

Reference to Table VI, in which the figures of Table V are grouped

TABLE VI.—*Slope at Various Ultimate Tensile Strength Levels.*

Ultimate Tensile Strength Level, tons/in.²	No. of Estimates.	Mean Value of Slope.
5	1	$1{\cdot}19 \cdot 10^4$
5½	6	1·13
6	8	1·11
6½	8	1·10
7	8	1·13
7½	6	1·12
8	3	1·11
8½	1	1·18
9	1	1·15

according to ultimate tensile strength level, reveals no evidence of such a variation; indeed, apart from the values at either end, for which only single estimates are available, the figures are remarkably constant about a mean of $1{\cdot}12 \cdot 10^4$.

4. *Effect of Cold Work.*

In their paper, Anderson and Mehl [4] showed that the rate of recrystallization was raised with increasing amounts of deformation. This has been confirmed in two series of experiments. In the first, three samples of chill-cast metal of composition *A*, which had been cold rolled to reductions of 20, 28, and 75% subsequent to annealing, were annealed for varying periods at 325° C. The resulting tensile strengths are plotted in Fig. 5. It will be seen that, as reported by Anderson and Mehl, the rate of softening is markedly increased with increasing amounts of cold work. A further point of interest is the difference in the tensile strengths of the fully recrystallized metal, which can only be due to variations in grain-size (90, 500, and 3000 grains/mm.², respectively).

In the second series, portions of a hot-rolled blank (analysing 0·19% silicon, 0·48% iron) were rolled down cold, without annealing, to thicknesses of 0·080, 0·064, 0·048, 0·036, and 0·020 in., giving reductions of 60, 68, 76, 82, and 90%. The isothermal annealing curves at 220° C. are given in Fig. 6. From these it will be seen that, although the curves are steeper the greater the cold reduction, they do not cross, as did those of the first series, so that the time required for complete softening was the same for all samples. In this case the final value for the tensile strength is the same for all samples, all being fine grained.

It would therefore seem that up to about 60% reduction cold work accelerates the softening process, but that cold work in excess of this has practically no effect.

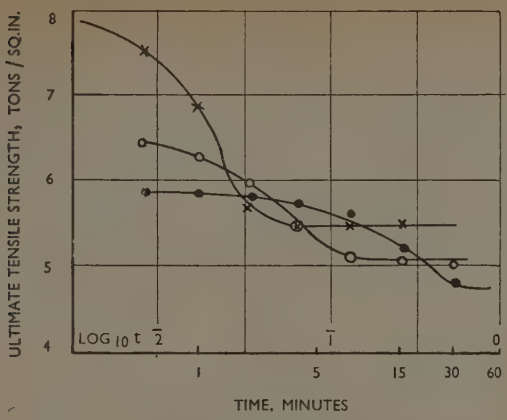

FIG. 5.—Effect of Cold Work on 325° C. Annealing Curves.

—●— 20% cold work.
—○— 28% „
—×— 75% „

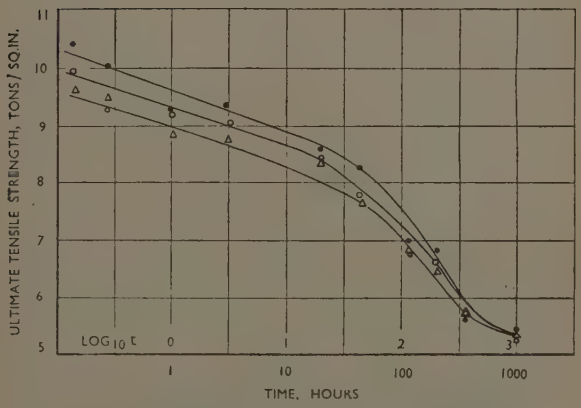

FIG. 6.—Effect of Cold Work on 220° C. Annealing Curves.

Final thickness.

—●— 0·020 in.
—○— 0·048 in.
—△— 0·080 in.

Other gauges not drawn owing to crowding.

5. *Effect of Hot-Working Temperature and of Soaking.*

In order to investigate the influence of the hot-working temperature and of prolonged soaking of the cast block at elevated temperatures, a number of continuously cast blocks, of identical commercial purity (namely 0·19% silicon, 0·48% iron) were heated to nominal temperatures of 420° and 520° C., respectively; half of the blocks were held at temperature for approximately one hour before hot working, while the other half were soaked for approximately 48 hr. at temperature. In all cases, hot working commenced immediately on removal from the furnace.

An additional variable in the shape of a process anneal at 0·2 in. thickness was also introduced for half the blocks of each type, the maximum metal temperature being 420° C., all metal being finally cold rolled to 0·036 in.

Details of the metal, together with the tensile-strength figures as rolled, are given in Table VII, while the isothermal annealing curves at

TABLE VII.—*Metal Used for Experiments on Hot-Working Temperature.*

Identity.	Hot-Working Temperature, ° C.	Time in Heating Furnace, hr.*	Process-Annealing Temperature, ° C.	Ultimate Tensile Strength, as Rolled, tons/in.²
*A*1	425°	47	nil	11·79
*A*2	425°	47	420°	10·49
*A*3	530°	50	nil	12·24
*A*4	535°	50	420°	10·88
*A*16	425°	4	nil	12·14
*A*6	405°	5½	420°	10·84
*A*15	510°	8	nil	12·04
*A*8	500°	9	420°	11·30

* Includes heating-up time.

220° C. are plotted in Fig. 7 for the metal soaked and hot worked at 420° C. and in Fig. 8 for that soaked and hot worked at 520° C.

In considering these results, allowance must be made for the variations in tensile strength as rolled, due to the wide variations in processing conditions. These differences are smaller than might have been expected, but the process-annealed metal is in every case of lower tensile strength than the corresponding hard-rolled metal.

The various annealing curves for each hot-working temperature are sensibly parallel, but neither the spacing nor the order is the same as the spacing and order of the tensile strengths in the as-rolled condition. A similar discrepancy was noted earlier in this paper when discussing the effect of a process anneal (p. 189). It would appear that it is due to some change in the rate of recovery during the very early stages of the

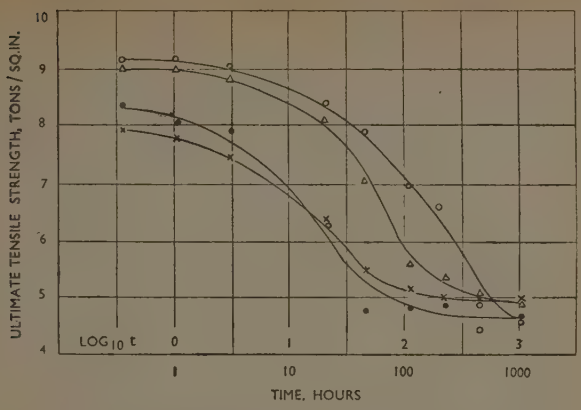

FIG. 7.—Effect of Process Variables on 220° C. Annealing Curves. Hot-working temperature, 420° C.

—×— Soaked, no process anneal.
—●— Soaked, process anneal.
—Δ— Not soaked, no process anneal.
—○— Not soaked, process anneal.

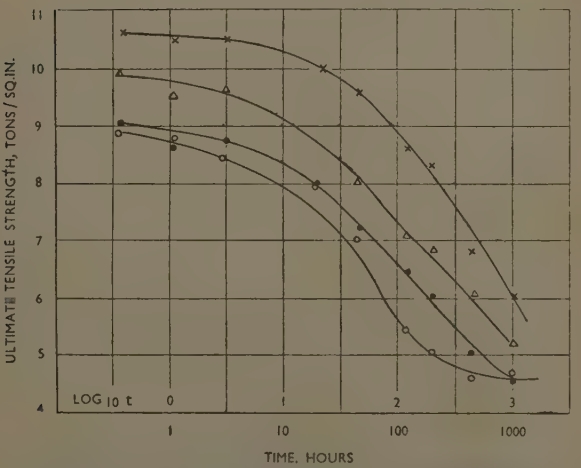

FIG. 8.—Effect of Process Variables on 220° C. Annealing Curves. Hot-working temperature, 520° C.

Key same as for Fig. 7.

softening process. These differences are tabulated in Tables VIII and IX, from which it will be seen that there is a certain amount of regularity in the behaviour of the metal.

In Fig. 8, for a hot-working temperature of 520° C., the two lower curves are those for metal which was process annealed and therefore had the lowest tensile strength in the as-rolled condition. The vertical

TABLE VIII.—*Effect of Process Anneal: Differences in Ultimate Tensile Strength, tons/in.*^{2}

	Hot-Working Temperature.			
	520° C.		420° C.	
	S–SA.	*N–NA.*	*S–SA.*	*N–NA.*
As rolled . . .	1·3	0·7	1·3	1·3
Partially annealed . .	1·9	1·0	−0·3	−0·2
Difference . . .	0·6	0·3	−1·6	−1·5

S = Soaked. *N* = Not soaked.
SA = Soaked with process anneal. *NA* = Not soaked with process anneal.

TABLE IX.—*Effect of Soaking: Differences in Ultimate Tensile Strength, tons/in.*^{2}

	Hot-Working Temperature.			
	520° C.		420° C.	
	S–N.	*SA–NA.*	*S–N.*	*SA–NA.*
As rolled . . .	0·2	−1·1	−0·3	−0·3
Partially annealed . .	0·9	0·2	−1·3	−1·5
Difference . . .	0·7	1·3	−1·0	−1·2

S = Soaked. *N* = Not soaked.
SA = Soaked with process anneal. *NA* = Not soaked with process anneal.

spacing between these and the corresponding curves for metal with no process anneal is, however, somewhat greater than the observed difference in tensile strength before annealing, indicating more rapid softening of the process-annealed metal. On the other hand, in Fig. 7, for a hot-working temperature of 420° C., the order of the curves is quite different, those for the process-annealed metal being in each case higher than for corresponding metal not so annealed, so that in this case softening has been slower after a process anneal.

A similar phenomenon can be observed with regard to the effect of

soaking at the two different temperatures. Here again the order and spacing of the curves differ from those of the tensile strengths in the as-rolled condition. In this case it would appear that soaking at 420° C. accelerates the subsequent softening on annealing, while soaking at 520° C. retards it. Further comparison of Figs. 7 and 8 shows that, in general, softening has been much more rapid for metal worked at the lower of the two temperatures.

6. *Onset of Recrystallization.*

With a view to determining the point on the softening curves at which the first signs of recrystallization could be detected, representative samples of chill-cast and continuously-cast metal, both with and without a process anneal, and of compositions *A* and *D*, were annealed for

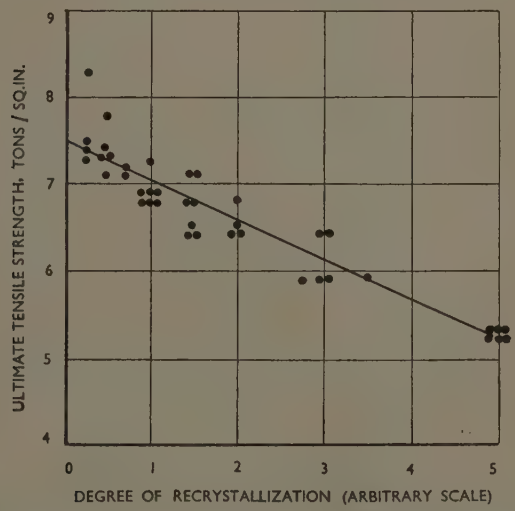

Fig. 9.—Variation in Ultimate Tensile Strength with Degree of Recrystallization.

varying times at 240° and 260° C., and X-ray diffraction patterns prepared by the transmission method, using molybdenum radiation. The degree of recrystallization was assessed on an arbitrary scale and is plotted against tensile strength in Fig. 9. In the arbitrary scale of recrystallization, 0 corresponds to completely unrecrystallized metal while 5 indicates the completion of the process. Thus, an assessment

of ½ means that a very few small sharp spots indicative of new crystals are visible on the pattern.

It will be seen that the points fall on a surprisingly good straight line, which indicates that recrystallization, as distinct from recovery, sets in at a tensile strength of 7½ tons/in.^{2} and that this is so irrespective of the previous history of the sample.

Thus, before recrystallization can be initiated in hard aluminium, it is necessary that recovery shall have proceeded to a definite stage, which is characterized by a tensile strength of 7½ tons/in.^{2} Further heating results in a progressive decrease in the tensile strength proportional to the degree of recrystallization. No evidence was obtained of any changes in structure during the purely recovery part of the process.

IV.—Discussion.

The form of the isothermal annealing curves is interesting in that the logarithmic plotting with respect to time has shown that for aluminium the two processes of recovery and recrystallization take place at any temperature, and that the only difference introduced by an alteration in the temperature is in the rapidity with which the process is accomplished. By stopping the anneal at a suitable instant, it is possible to obtain a large measure of recovery with no detectable signs of recrystallization, but it seems to be impossible to initiate recrystallization without prior recovery and without passing through a state where the mechanical properties appear to be fairly stable when plotted against time (but not when plotted against a logarithmic-time scale).

Burgers,[1] in putting forward his theory that both recovery and recrystallization are due to different stages in the process of diffusion and mutual cancellation of dislocations of the lattice structure, finds it difficult to account for the different "rest values" of the elastic limit found by Kornfeld[2] after anneals at different temperatures. From the evidence presented in this paper it seems that these have no real existence, and it is furthermore shown that, with hard aluminium, before recrystallization commences, recovery proceeds to the same point, as judged by mechanical properties, irrespective of temperature of anneal or previous history of the metal.

Another point which Burgers finds difficult to explain is the apparent discrepancy between the observations of Kornfeld, that higher "rest values" were obtained with more heavily cold-worked metal, and those of other workers, such as Anderson and Mehl,[4] Sauerwald,[5] and Brindley,[6] that recrystallization is more rapid the greater the degree of cold work. Reference to Fig. 5 shows that again the discrepancy is

illusory, in that with prolonged annealing the curves cross one another so that the specimen with the smallest amount of cold work is the last to recrystallize, although it has the lowest "rest value".

Further, it has been shown that the time required to reach a definite stage in the process of recovery and recrystallization is related to the absolute temperature by a relation of the form :

$$\log ct = \frac{Q}{RT}$$

where t is the time, T the absolute temperature, R the gas constant, Q the over-all activation energy of the whole process, and c a constant proportional to the atomic frequency.

The figures given in Table V show that the slope of the log t–$1/T$ line, and hence the value of Q, is the same irrespective of whether one is dealing with the purely recovery stage of the process or whether recrystallization has set in. The value obtained for Q is 51,240 cal./g. atom, which agrees well with the value of 52,100 cal. found by Anderson and Mehl [4] for metal with 15% deformation, and is also of the same order of magnitude as would be expected for the activation energy of self-diffusion of aluminium (a figure of 37,500 cal./g. atom has been calculated [7]). Anderson and Mehl found that the activation energy decreased with increasing cold work up to 15%, the maximum level studied. It now appears that with 30% cold work or more, the value is sensibly constant, the asymptotic value being slightly lower than that found by the American workers for 15% cold work.

That the activation energy of the process is sensibly the same whether it is measured at the recovery stage or after the onset of recrystallization suggests that the two processes are similar in their nature. Both probably involve the diffusion of dislocations through the lattice and the annihilation of those of opposite sign, the additional activation energy involved in the formation of new crystals being too small to be detected by the methods adopted.

It is of interest to note that the various process variables studied, while having little or no effect on the activation energy of the process, may have a marked effect on the rate of softening. The simple difference between the two hot-working temperatures may be ascribed to the greater amount of silicon in solid solution at the higher temperature, but this explanation does not account satisfactorily for the complex effects of soaking and process annealing. For example, experiment shows that silicon is present in supersaturated solid solution in a continuously cast block and that precipitation takes place both at 520° and 420° C. Therefore, there will be, at either temperature, less silicon in solid solution in

the soaked than in the unsoaked blocks, yet the effect of soaking is in opposite senses at the two temperatures. It is clear that the explanation of the phenomena is more complex, and so far no satisfactory theory has been developed which will account for all the observations.

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HIGH-TEMPERATURE TENSILE PROPERTIES OF CAST ALUMINIUM–SILICON ALLOYS AND THEIR CONSTITUTIONAL SIGNIFICANCE.* 1152

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Synopsis.

The tensile properties at high temperatures of some aluminium–silicon alloys were determined (*a*) during cooling from the liquid state and (*b*) after rapid reheating of chill-cast alloys. Strength–temperature curves relating to both conditions were obtained for ten alloys containing from 0 to 12% silicon.

The curves consist of a relatively low-temperature portion in which the alloys are ductile and in which the strength falls gradually as the temperature is increased, and a steeper high-temperature portion in which the alloys fracture in a brittle, intercrystalline manner until a temperature is reached when so much liquid is present in the mass that coherence is lost.

The results are discussed, and an appraisal is made of the effects of various factors on the form of the strength–temperature curve. The point of discontinuity in the curve was found to be associated with the effective solidus temperature, and the position of the point of non-coherence to be a function of the proportion of liquid in the alloy. The interval between these temperatures, i.e. the brittle range, was correlated with the tendency to cracking during casting and welding. With any alloy, the extent of the brittle range is less as determined by tensile testing after rapid heating from the solid state than by testing during cooling from the liquid state. This difference is ascribed to differences in crystal size rather than to the different thermal conditions obtaining in the two tests.

I.—Introduction.

The object of the majority of investigations into the mechanical properties of alloys is to ascertain the limits of their endurance in the various practical uses to which they may be put. In consequence, few such investigations are made at temperatures approaching the melting point of the metal under consideration, although a knowledge of the strength and ductility of alloys at these temperatures is of great importance in many commercial operations. Among such operations may

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be mentioned forging and rolling, and particularly those, such as welding and casting, which involve fusion of the metal.

A number of investigators have determined the mechanical properties of aluminium alloys with the object of relating these properties with the tendency to crack during casting and welding, a defect to which aluminium alloys are particularly prone owing to their high coefficient of expansion. Archbutt, Grogan, and Jenkin [1] determined the impact resistance at elevated temperatures of several commercial alloys of aluminium, and found that, in most cases, the resistance to shock was very low at the point of incipient fusion. It was postulated by these workers that alloys in which there was a rapid increase in impact resistance with fall in temperature immediately below the solidus, would have a lower susceptibility to cracking than alloys in which the increase was more gradual.

Verö [2] examined the tendency to cracking at elevated temperatures of a number of aluminium alloys, including a series of aluminium–silicon alloys, by means of a casting test, and attempted to relate the results with the tensile properties at high temperatures. For the determination of the tensile properties a bend test was employed in which a cylindrical specimen, supported at each end, was centrally loaded and gradually heated until fracture occurred.

Although the values obtained by Verö for the relative tendencies to high-temperature cracking of aluminium–silicon alloys are somewhat at variance with the findings of later workers,[3] his failure to correlate such values with the high-temperature properties would seem to be due to his choice of method for the determination of these properties. The use of a bend test is open to the objection that loading is non-uniform, and testing on a rising temperature is conducive to the development of temperature gradients within the specimen.

A greatly improved experimental technique was used by Singer and Cottrell,[4] who determined the tensile properties of a series of ten aluminium–silicon alloys at temperatures both above and below the equilibrium solidus. The alloys were tested at a constant rate of straining and at constant temperature, after being maintained at the temperature of testing for a time regarded as sufficient for the attainment of structural equilibrium. Singer and Cottrell found that with all the alloys there was a sudden fall in strength and complete loss of ductility at the point of incipient fusion. Above this temperature, the alloys broke with brittle, intercrystalline fractures, and the extent of the brittle range—the range of temperatures between the solidus temperature and the temperature at which the alloy lost all coherence—was found to vary with the silicon content. The theory of cracking at

elevated temperatures advanced as a result of this and later work[3] established a relationship between the constitutional diagram for aluminium–silicon alloys and their tendency to crack at temperatures above the solidus.

By assuming that similar brittle ranges exist in other aluminium alloy systems, the theory has since found a wider application.[5, 6, 7] Various discrepancies between the theory and experimental results have been ascribed to departures from structural equilibrium which alter the effective position of the solidus and so modify the extent of the range over which brittle fracture occurs. For this reason it was felt that an investigation into the high-temperature tensile properties of alloys not in structural equilibrium would be of value. The present work has been carried out on a series of aluminium–silicon alloys containing up to 12% silicon, and two tests have been devised for determining the tensile properties of the alloys at elevated temperatures in conditions similar to those which obtain during casting and welding.

II.—Experimental Work.

Both casting and welding involve the solidification of liquid metal, while welding involves, in addition, the rapid heating of solid metal to its point of fusion. In order to determine the properties of a material in these two conditions, it is clearly necessary to use two different tests. The results of the first will be applicable to casting processes, while an understanding of the welding operation will necessitate a consideration of the results of both tests; the two tests devised for this purpose in the present investigation are described below.

1. *Preparation of the Alloys.*

The tests were carried out on super-purity aluminium and nine alloys containing nominally 0·1, 0·25, 0·6, 1·0, 1·5, 2, 4, 8, and 12% silicon, the alloys being prepared from super-purity aluminium and a 20% aluminium–silicon temper alloy of high purity. The flux used in the melting was a 2 : 1 mixture of sodium chloride and sodium fluoride: in certain conditions this flux can exert a modifying influence on aluminium–silicon alloys, but in the present work the quantities of flux involved (approximately $\frac{1}{4}$ g. of flux to 25 g. of metal) were too small for any such effect to be appreciable. The alloys were chill cast with a super-heat of 100° C. into ingots measuring $6 \times 1\frac{3}{4} \times \frac{3}{8}$ in. One half of each batch of alloy was used in each of the two tests.

Chemical analysis of the alloys indicated that the actual analyses were in close agreement with the nominal compositions with respect to silicon content, and it was found also that the iron contents were low,

consistent with the use of super-purity materials. The results of chemical and spectrographic analysis of the super-purity aluminium used as the base material for the manufacture of the alloys are given in Table I.

TABLE I.—*Analysis of Super-Purity Aluminium.*

Silicon, %.	Iron, %.	Copper, %.	Magnesium, %.
0·005	0·0015	0·0005	0·005

The macrostructure of each of the cast alloys was examined before testing by preparation of a section taken from the lower end of one ingot of each alloy.

2. *Testing of Alloys During Cooling from the Liquid State.*

A test, which will hereafter be referred to as the direct-casting test, was designed for determining the tensile properties of aluminium alloys at temperatures both above and below the solidus during cooling from the liquid state. In this test, the metal, at a known degree of superheat, was cast into a small stainless-steel mould in which the mould cavity, viewed from above, consisted of a totally-enclosed rectangular central section with two wedge-shaped prolongations open at the top. The mould was made in two halves, and at a pre-determined stage in the cooling the two halves were pulled apart in a tensometer of standard design, and a measurement made of the load required to fracture the semi-solid mass within the mould. The temperature of the metal in the mould was measured by means of a Chromel–Alumel thermocouple arranged to record the temperature of the casting near to the point of fracture.

A motor drive was fitted to the tensometer, and a set of interchangeable gears permitted the use of a variety of testing speeds. Most of the tests, however, were carried out at a cross-head speed of 1 in./min., and it was found possible to record with accuracy loads down to 1 lb., equivalent to a stress on the specimen of about 8 lb./in.^{2} A general view of the apparatus is given in Fig. 2 (Plate XV) and a diagram of the cast test-piece in Fig. 1(*a*).

In all the tests the casting temperature was standardized at 100° C. above the liquidus of the particular alloy considered; and by heating the mould before casting to a temperature approximately 100° C. below that at which it was desired to determine the tensile strength, it was found that the rate of cooling of the cast metal was sufficiently slow 2 min. after casting for the tensile strength to be determined under conditions

which were approximately isothermal. In all the tests, therefore, the tensile strength of the alloy was determined after the lapse of 2 min. from the moment of pouring the metal into the mould, previously heated to the necessary temperature.

Preliminary measurements indicated that under the cooling conditions operative during the test there were no appreciable temperature gradients across the section or along the length of the cast test-piece, and no difference in temperature between the inner wall of the mould and the casting.

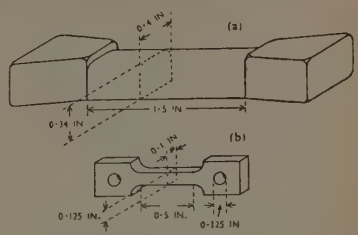

FIG. 1.—Diagrams of Test-Pieces Used in (*a*) Direct-Casting Test, and (*b*) Reheated-Casting Test.

There was no tendency for the test-pieces to be drawn through the tapered ends of the mould, even with the most ductile alloys.

3. *Testing of Alloys Heated from the Solid State.*

An apparatus was designed for the tensile testing of material heated rapidly in a lead bath to a temperature in the region of the solidus and tested after a few seconds at that temperature. In this test, which will be referred to subsequently as the reheated-casting test, the test-piece was of the design conventionally used for the tensile testing of material in sheet form; the dimensions of the test-piece are given in Fig. 1(*b*). Because of this design, it was found possible to test alloys in the apparatus at temperatures as low as 400° C.; and measurements were made of the strengths and elongations of the alloys between 400° C. and the temperatures at which the strengths fell to an unmeasurable value.

For the purposes of comparison with the results of the direct-casting test, cast specimens were used in the reheated-casting test, although it is appreciated that in industrial practice the majority of welding is done on wrought material. Cast material is more inhomogeneous than wrought material, so that, as will be apparent from the discussion, a consideration of the results obtained in the present investigation should provide some indication of the worst conditions likely to be encountered during the welding of aluminium alloys.

A general view of the apparatus is given in Fig. 3 (Plate XV). The mechanism for applying and measuring the load on the specimen was contained in a frame arranged to slide on a vertical column to enable the test-piece to be lowered into the lead bath. The specimen was held in this mechanism by means of two light steel grips, the lower

of which was attached to the main frame of the testing machine, while the upper was connected through a light framework which housed the load-indicating mechanism to a screwed rod and handle at the top of the main frame. The load was applied manually to the specimen by means of the handle, and was balanced against a steel beam arranged to take the full load at its central point. The deflection of the beam was magnified hydraulically by means of a cylindrical reservoir of mercury enclosed at the top by a rubber diaphram connected to the centre of the beam (see Fig. 4, Plate XVI). Movement of the diaphragm caused the mercury to flow along a graduated glass capillary tube, and the use of three such capillaries of different internal diameter, calibrated by the application of known loads to the machine, permitted measurement of loads in the ranges 0–9, 0–25, and 0–100 lb., respectively. The sensitivity of the machine was of the order of 0·2 lb. on the 0–9 lb. scale, corresponding to a stress of about 16 lb./in.^{2} on the specimen.

The temperature of the specimen was assumed to be that of the lead bath and was measured by means of a Chromel–Alumel thermocouple protected by a stainless-steel sheath and located as close as possible to the central portion of the test-piece. Measurement of the rate of rise of temperature of the specimen when immersed in the bath revealed that the temperature of the specimen rose to within 10° C. of that of the bath some 10 sec. after immersion, and that the actual bath temperature was attained after 14 sec.

Before testing, a 0·5-in. gauge-length was scribed on each specimen, and the test was commenced 20 sec. after immersion of the specimen in the bath, the rate of straining being maintained approximately constant at 1 in./min., as in the direct-casting test.

The temperature of the lead bath was observed to fall 5°–15° C. on the introduction of the specimen, but remained practically constant throughout the testing operation. A reading of the temperature was taken at the point of maximum stress.

The reproducibility of the results was good, particularly in the case of alloys not subject to casting flaws, and microscopic examination of a large number of specimens after immersion in the lead bath revealed that no penetration of lead into the surface of the specimen had occurred during the period of testing. This is illustrated by Fig. 6 (Plate XVII), which shows the appearance of the lead film on the surface of a typical specimen after completion of a high-temperature test.

III.—Experimental Results.

A number of the experimental results are recorded in Figs. 12–20; of these, Figs. 12–17 show the strengths of six of the ten alloys examined,

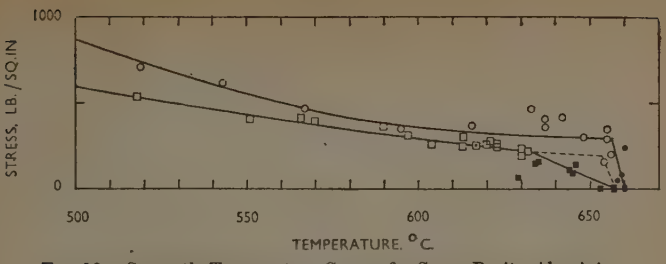

FIG. 12.—Strength–Temperature Curves for Super-Purity Aluminium.

Key to Figs. 12–17.

Direct-casting test { □ Ductile fracture. ▣ Semi-ductile fracture. ■ Brittle fracture

Reheated-casting test { ○ Ductile fracture. ● Brittle fracture.

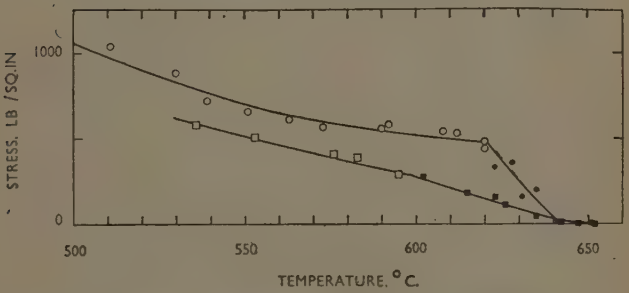

FIG. 13.—Strength–Temperature Curves for 0·25% Silicon Alloy.

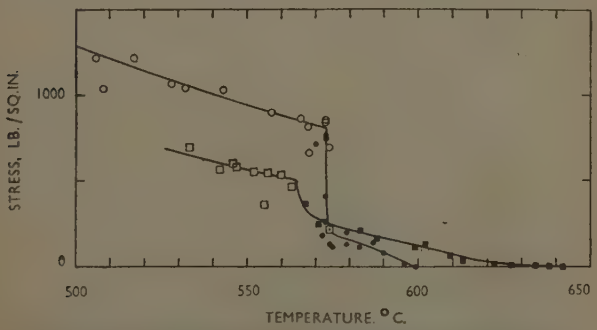

FIG. 14.—Strength–Temperature Curves for 1·0% Silicon Alloy.

at temperatures above 500° C., in the conditions of each test and illustrate the difference in the behaviour of an alloy in the two tests. The symbols used in the construction of Figs. 12–17 are defined in Fig. 12.

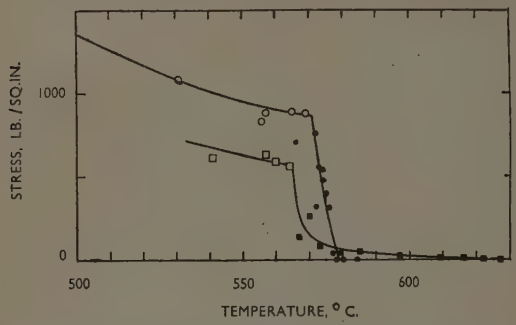

Fig. 15.—Strength–Temperature Curves for 2% Silicon Alloy.

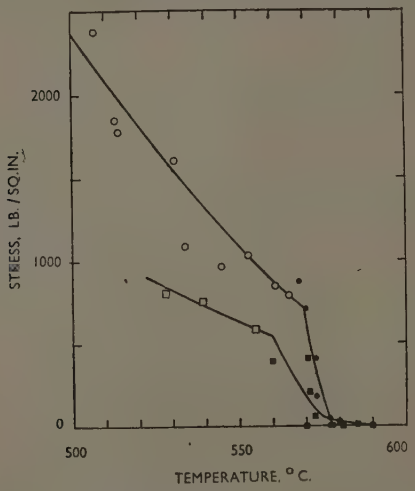

Fig. 16.—Strength–Temperature Curves for 4% Silicon Alloy.

The tensile results obtained with the reheated-casting test are plotted graphically in Fig. 18, which shows the general form of the strength–temperature curves for the alloys over the temperature range between 400° C. and the temperature at which the strength fell to zero. The

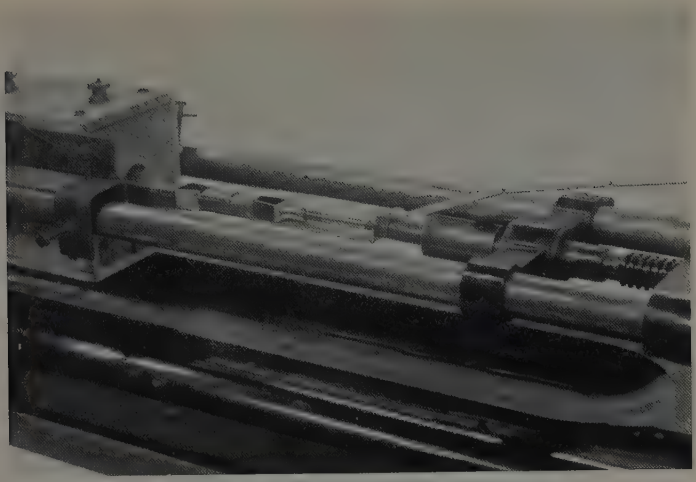

FIG. 2.—General View of Apparatus for Direct-Casting Tests.

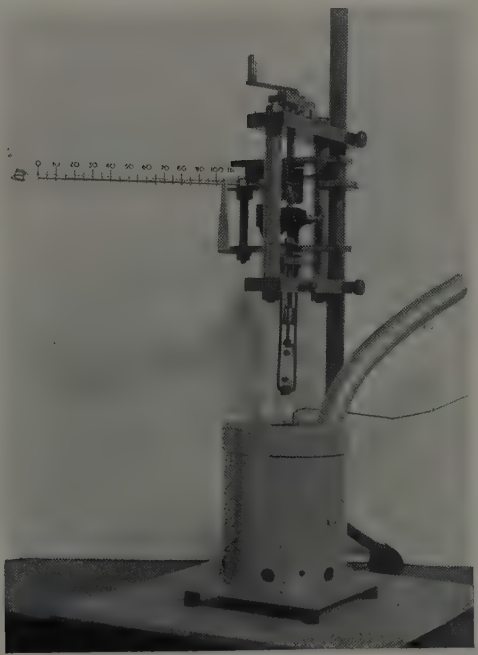

Fig. 3.—General View of Apparatus for Reheated-Casting Tests.

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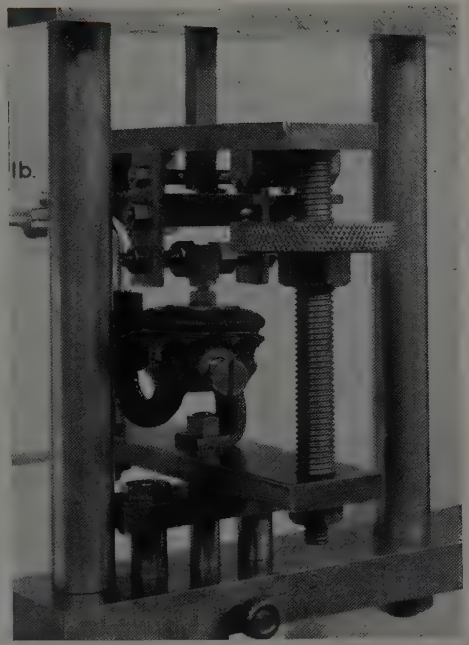


Fig. 4.—Load-Indicating Mechanism in Reheated-Casting-Test Apparatus.

Fig. 5.—Surface of Fracture in Alloy Containing 2·0% Silicon, Tested at 565° C. in Reheated-Casting Test. Unetched. × 30.

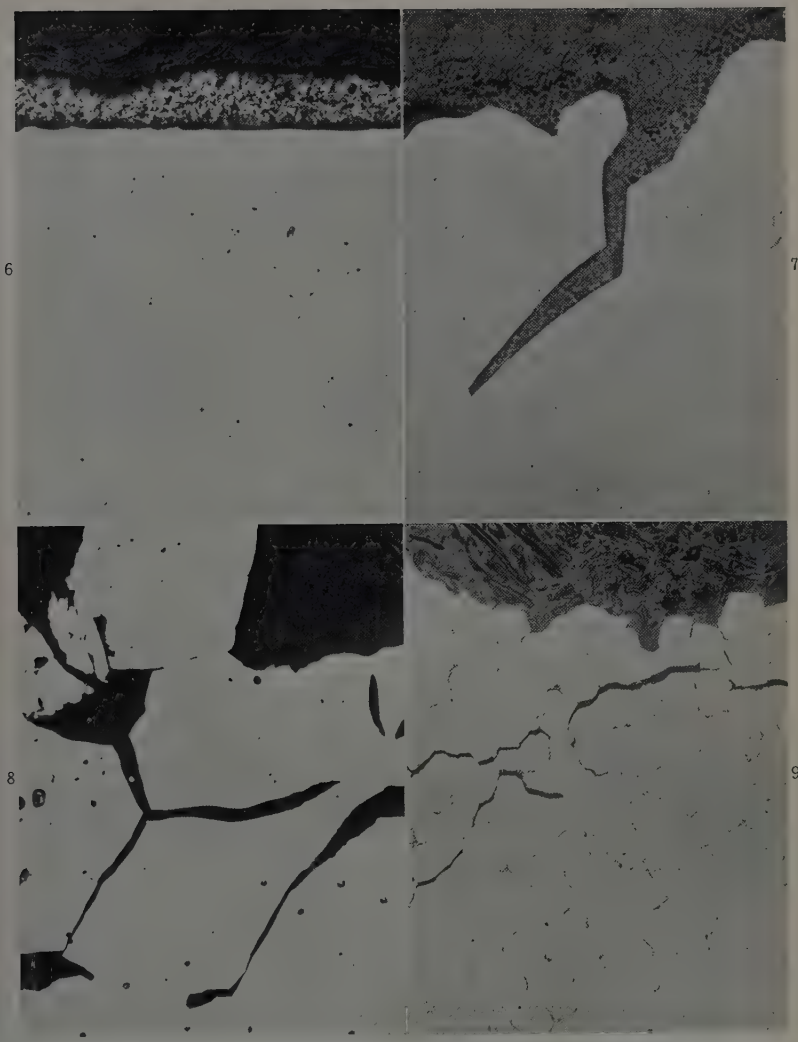
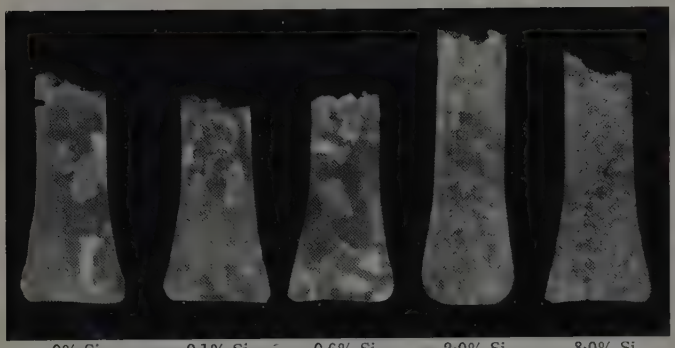


FIG. 6.—Surface Region of Alloy Containing 0·1% Silicon After Immersion in Lead Bath at 643° C. Unetched. × 150.

FIG. 7.—Surface of Fracture in Alloy Containing 0·1% Silicon, Tested at 643° C. in Reheated-Casting Test. Unetched. × 90.

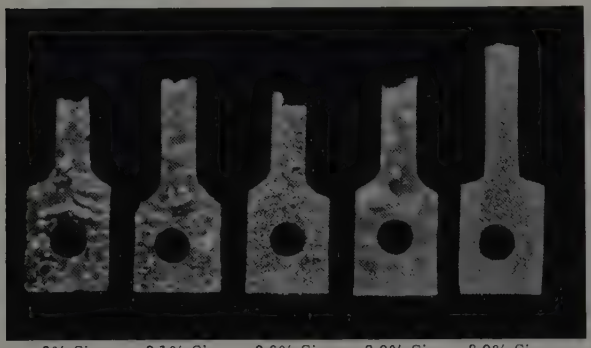
FIG. 8.—Surface of Fracture in Alloy Containing 0·6% Silicon, Tested at 559° C. in Direct-Casting Test. Unetched. × 90.

FIG. 9.—Surface of Fracture in Alloy Containing 2·0% Silicon, Tested at 572° C. in Reheated-Casting Test. Etched in 0·5% HF. × 90.



0% Si. 0·1% Si. 0·6% Si. 2·0% Si. 8·0% Si.

FIG. 10.—Macrostructure of Direct-Casting Test Specimens. × 1.



0% Si. 0·1% Si. 0·6% Si. 2·0% Si. 8·0% Si.

FIG. 11.—Macrostructure of Reheated-Casting Test Specimens. × 1·5.

more important results obtained with all the alloys in both tests are summarized in Table II. Two typical elongation–temperature curves are plotted in Figs. 19 and 20.

1. *General Observations.*

As illustrated by the curves in Figs. 12–17, certain characteristics are common to every alloy examined in either condition of testing.

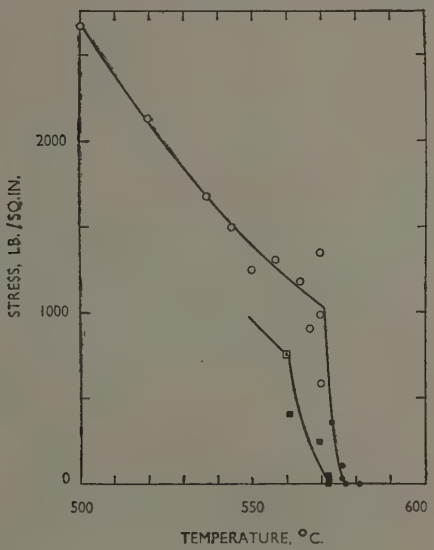


FIG. 17.—Strength–Temperature Curves for 12% Silicon Alloy.

The strength–temperature curves consist of two parts, a low-temperature portion over which there is a gradual decrease in strength with rise in temperature, and a high-temperature portion associated with a steeper decline. Moreover, in the low-temperature region the rate of change of strength with respect to temperature falls evenly as the temperature rises, but in the high-temperature range no generalization of this nature can be made, and the form of the curve varies greatly from alloy to alloy.

In the low-temperature range the alloys were all characterized by a high ductility, and while, in many test-pieces, the fractured surfaces were of cup and cone form, others extended virtually to a point. In the direct-casting test there was a tendency for ductile test-pieces to break with a jagged fracture instead of drawing down to a point, particularly

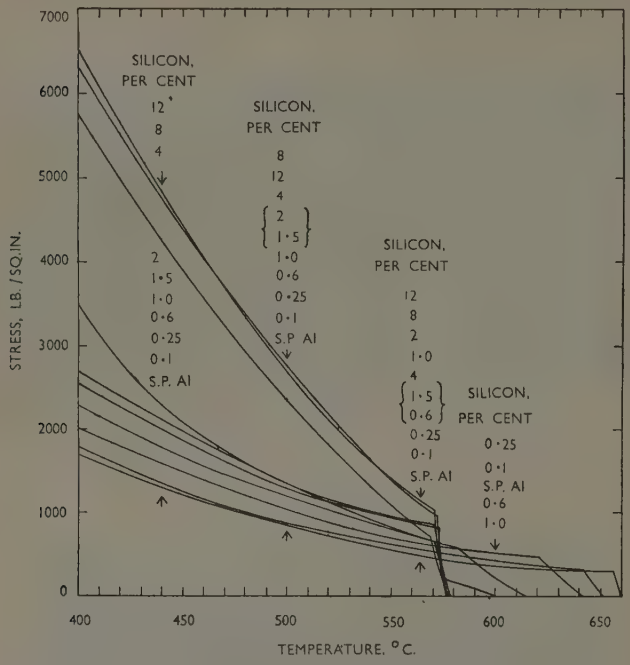


Fig. 18.—Strength–Temperature Curves for Chill-Cast Aluminium–Silicon Alloys.

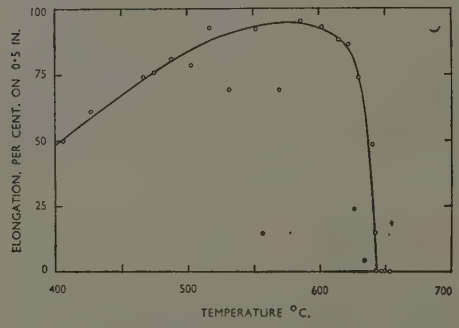


Fig. 19.—Elongation–Temperature Curves for 0·1% Silicon Alloy.

TABLE II.

Alloy.	Temperature of Embrittlement, ° C.			Temperature of Non-Coherence, ° C.			Temperature of "2% Coherence", ° C.			Per cent. Liquid at Temperature of 2% Coherence.			Temperature Range Between Point of Embrittlement and 2% Coherence, ° C.		
	D.	*R.*	*S* and *C.*	*D.*	*R.*	*S* and *C.*	*D.*	*R.*	*S* and *C.*	*D.*	*R.*	*S* and *C.*	*D.*	*R.*	*S* and *C.*
Super-purity aluminium . .	633	656	655	657	660	659	657	660	659	...	...	...	24	4	4
0·1% silicon . .	622	642	645	652	652	657	651	652	653	9	5	9	29	10	8
0·25% silicon . .	599	621	641	652	642	653	650	642	650	18	5	9	51	21	9
0·6% silicon . .	556	582	622	644	615	652	639	614	645	19	4	20	83	32	23
1·0% silicon . .	564	573	605	640	599	649	630	597	632	22	6	17	66	24	27
1·5% silicon . .	564	571	578	635	578	637	621	578	621	25	...	18	57	7	43
2% silicon . .	565	571	577	627	579	635	610	579	607	26	...	15	45	8	30
4% silicon . .	560	569	575	589	577	606	584	577	584	...	...	25	24	8	9
8% silicon . .	562	572	574	575	577	578	573	577	578	...	...	...	11	5	4
12% silicon . .	561	571	576	572	577	578	572	577	578	...	...	...	11	6	2

D = Direct-casting test.
R = Reheated-casting test.
S and *C* = Results obtained by Singer and Cottrell.[4]

in the alloys of higher silicon content. These fractures were, however, considered to exhibit the same essential features as the more perfect examples.

The discontinuity in the strength–temperature curves was associated with a relatively sharp change in the type of fracture from ductile to brittle and intercrystalline. Fractures of this latter description occurred at all higher temperatures at which the alloy retained any measurable strength. At temperatures nearer the liquidus there was a gradual change to a glazed type of fracture, indicating the presence of much liquid in the test-piece.

In drawing the curves in Figs. 12–17 and the curves from which the results recorded in Table II were abstracted, the results for specimens containing any obvious casting defects were disregarded, so that the curves as drawn are applicable to sound material.

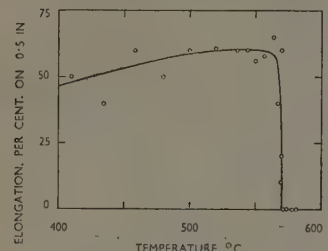


FIG. 20.—Elongation–Temperature Curves for 12% Silicon Alloy.

Measurements of elongation over the 0·5-in. gauge-length marked on the reheated test-pieces, although subject to considerable scatter, enabled an elongation–temperature curve to be drawn for each alloy tested. Since the results for obviously unsound specimens were discarded, the scatter in the elongation results was too great to be ascribable solely to casting defects, and may possibly have been due to variations in crystal size and orientation. The elongation curves were all of the same basic form, those for two representative alloys being shown in Figs. 19 and 20. With increase in the temperature of testing there was, with every alloy, a steady increase in elongation to a maximum value, followed by a gradual and then a much steeper decline in elongation with further increase in temperature. At temperatures above the point of embrittlement, the ductility varied from zero to a maximum of 3%.

The change in properties from a state of ductility to one of brittleness was not absolutely sharp, but occurred over a small temperature range; and in the reheated-casting test there were instances of test-pieces which elongated to the extent of about 20% and then broke with a brittle fracture without any tendency to neck down to a point.

In the direct-casting test it was not possible to make accurate measurements of elongation owing to the difficulty of marking a gauge-length on the specimens. Qualitatively, the variation of elongation

with temperature was similar to that in the reheated-casting test, although the transition from ductile to brittle fractures was more gradual. Intercrystalline tears were frequently found in test-pieces in which considerable extension had occurred. At progressively higher temperatures the number of these tears increased while the deformation undergone by each crystal lessened, until, finally, truly brittle fractures with little or no elongation were obtained.

2. *Macrostructure of the Alloys.*

An examination was made of the macrostructures of test-pieces of super-purity aluminium and aluminium–silicon alloys containing 0·1, 0·6, 2, and 8% silicon, tested in both tests at temperatures above that corresponding to the discontinuity on the strength–temperature curve. The results of this examination are illustrated in Figs. 10 and 11 (Plate XVIII) which relate respectively to the direct-casting test and to the reheated-casting test. Alloys containing up to 0·6% silicon, after testing by the direct-casting method, were observed to possess a particularly coarse crystal structure which became progressively finer on the addition of further quantities of silicon. Although in Fig. 10 the crystals in each alloy appear to be equi-axed, it is clear that all the low-silicon alloys solidified directionally, since examination of the surfaces of the brittle fractures in such alloys revealed the presence of columnar crystals which had grown at right angles to the specimen surfaces and consequently met in four diagonal planes.

In the direct-casting test, the temperature of testing was controlled by adjustment of the mould temperature, and this adjustment, by influencing the degree of chilling in the different tests, was observed to have influenced the structures of the test-pieces of the alloys containing 1·0 and 1·5% silicon, some of which were columnar and some equi-axed. In alloys containing 2% silicon or more, the crystal habit was entirely equi-axed.

A comparison of the structures of the reheated test-pieces (Fig. 11, Plate XVIII) with those of the original ingots indicated that recrystallization of the test-pieces had occurred during the heating. Although complete recrystallization would seem to have taken place during the testing at high temperatures, it is probable that this process was incomplete at the lower temperatures at which a number of the tests were carried out. Thus, in super-purity aluminium specimens tested at 400°–450° C., the junction plane between the columnar crystals showed in relief as a line along the surface of the much extended gauge-length.

The structures illustrated in Fig. 11 exhibit a somewhat irregular

variation in crystal size with increasing alloy content, which can be attributed, in part at least, to a similar variation in the original ingots.

3. *Microstructure of the Alloys.*

Figs. 5, 7, 8, and 9 (Plates XVI and XVII) illustrate a number of points of interest arising out of the microscopic examination of the different test-pieces. In Figs. 7 and 8 are shown typical intercrystalline fissures in specimens tested in the two tests at temperatures above the point of embrittlement. It will be seen that the fissures in the reheated-casting test specimen (Fig. 7) are essentially the same as those in the directly-cast test specimen (Fig. 8).

The difference in the appearance under the microscope of ductile and brittle fractures is shown in Figs. 5 and 9 (Plates XVI and XVII). In both Figures, the structures are those of 2%-silicon alloy specimens tested by the reheated-casting method, the respective testing temperatures being 565° and 572° C. The ductile test-piece (Fig. 5) can be seen to have necked down to some extent, although complete fracture occurred when the reduction in area was still far short of 100%. There are, in this Figure, many instances of intercrystalline tears in association with deformed crystals, a frequent characteristic of tests carried out at temperatures just below the temperature of embrittlement.

The test-piece which broke with a brittle fracture (Fig. 9) shows no sign of deformation. The outline of the fracture clearly marks the boundaries of the undeformed crystals, and the internal fissures are located similarly at the crystal boundaries.

Attention was given to the question whether modification of the aluminium–silicon eutectic had occurred during the casting operation in either test. It was observed in a number of cases that the eutectic had the coarse and acicular appearance typical of an unmodified structure, but in other cases a much finer structure was apparent. It is doubtful whether complete modification occurred in any of the test-pieces or ingots used in the present investigation, since the quantities of sodium-bearing flux used in the melting operations were too small for modification to have been brought about in the normal manner. It is known, however, that rapid cooling from the liquid state produces a similar refinement of the eutectic, and the intermediate (i.e. partially refined) structures encountered in a number of instances during the present work were probably formed in this way. It may be cited in support of this contention that the chill-cast ingots, in general, possessed much finer eutectic structures than the more slowly cooled direct-casting test-pieces, and that specimens containing molten eutectic which were quenched in iced water gave the finest eutectic structures of all.

IV.—Discussion.

A number of observations were made by earlier workers on the relationship between strength * and temperature for members of a series of alloys at temperatures within and just below the freezing range. It was not until the work of Singer and Cottrell,[4] however, that suggestions were made regarding the effect of the constitution of the alloys on the nature of this relationship and that theoretically deduced curves relating strength and temperature were supported by experimental data. These latter workers formulated a series of hypothetical strength–temperature curves for a pure metal and for five typical alloys in a eutectic series based upon that metal. The principal assumptions made in constructing the hypothetical curves were essentially as follows :

(*a*) The strength of a solid metal or alloy falls gradually as the temperature is raised.

(*b*) The effect of the formation of liquid in the alloy is to lessen the quantity of solid material carrying the applied load, and hence to reduce the measured strength proportionately.

(*c*) When the proportion of liquid exceeds a certain critical value (not necessarily the same for every material), the alloy loses its coherence.

On the basis of assumption (*b*) it would be expected that any alloy which contains a eutectic phase will undergo a rapid fall in strength on being heated through the eutectic temperature, and on the basis of assumption (*c*) that the strength of each alloy in the series will fall to zero at some temperature between the solidus and the liquidus. A range of temperatures in which some members of the alloy series retain a proportion of their strength is implicit in the assumptions, and it would be expected, furthermore, that in this range the presence of liquid between the solid crystals would lead to intercrystalline fracture and low ductility. For a series of aluminium–silicon alloys tested in conditions of structural equilibrium, the hypothetical curves were in good agreement with those determined experimentally. If the above-stated assumptions can be taken as justified by reason of the agreement between the experimental and hypothetical curves, it follows that in every alloy (in a eutectic system) the effective solidus temperature must coincide with a discontinuity in the strength–temperature relationship. Solid alloys are likely to be ductile at high temperatures, and since ductility would be expected to be materially reduced by the first appear-

* The term strength is here considered to mean the maximum stress at a specified rate of straining.

ance of liquid between the solid crystals, it also follows that there is a sudden change in ductility on heating through the solidus temperature.

Singer and Cottrell plotted a curve showing the relationship between the silicon content of the alloys investigated and the temperature at which there was a sharp discontinuity on the strength-temperature curves. This curve was, in the main, closely correspondent with the known position of the solidus in the aluminium–silicon equilibrium constitutional diagram. There were, however, two points of dissimilarity, the first being that the discontinuity in the curve for super-purity aluminium was some 4° C. below the recognized melting point, and the second that the temperature of the eutectic horizontal was, on an average, 575·5° C., i.e. about 2° C. lower than the generally observed value. Singer and Cottrell were inclined to the view that, in the case of super-purity aluminium at least, the explanation of these phenomena was associated with the presence of traces of impurity at the crystal boundaries. It was suggested by Varley in the discussion of their paper, however, that the results might be evidence of " pre-melting " phenomena of the type previously observed by Chalmers,[8] i.e. that the crystal-boundary material might have, for purely physical reasons, a lower melting point than the crystals themselves, and that the observed temperature of embrittlement and fall in strength was, in reality, the temperature at which melting began in the crystal boundaries.

It would seem, therefore, that in conditions of structural equilibrium there is a close relationship between the temperature of incipient melting in an alloy and the temperature of embrittlement, i.e. the temperature at which the discontinuity occurs in the strength–temperature curve. It is hence of interest to consider the factors which influence this critical temperature and which determine the characteristics of the strength–temperature curves of alloys tested in conditions which do not permit of the attainment of structural equilibrium.

1. *Temperature of Embrittlement.*

The temperature at which embrittlement occurs in an alloy is dependent on a number of factors :

(a) *Effect of Rapid Solidification.*

The attainment of structural equilibrium in an alloy at any given temperature is a time-dependent process. At normal rates of solidification, few alloys, if any, approach this condition, and the degree to which a solid alloy departs from equilibrium is a function of the rate of cooling from the liquid state. The term " rapid solidification " is clearly only relative, and in the present consideration will be taken to mean solidi-

fication at such a rate that no pronounced diffusion of solute atoms can occur in the solid metal.

It can be shown that, when there is no diffusion of solute atoms, every rapidly solidified alloy (in a eutectiferous system) contains, when solid, a certain proportion of eutectic. This is due to the fact that a solid solution is always poorer with respect to the solute element than the liquid from which it separates, and that homogenization in the solid state can only take place by a process of diffusion. This result is of little importance in itself, but the argument can be extended to show that even in practical conditions of solidification, in which partial but not complete diffusion occurs, any alloy in a eutectic system must contain some eutectic phase, however little of the solute element is present.

The mathematical treatment of the solidification process is somewhat complex owing to the variable composition of the deposited solid. In order to formulate a relationship between the proportions of solid and liquid phases present during solidification, a knowledge of the average composition of the former is essential. This difficulty can, however, be overcome by using a method of self-consistency developed by one of the present authors (Jennings), in which the unknown value is estimated and the results of the calculations used to check the original estimate. By this means the proportion of eutectic present in the solid alloy may be calculated if it is assumed that no diffusion occurs in the solid state, and in addition it is possible to determine the volume of primary solid solution deposited from the liquid during cooling between any two temperatures.

By assuming that the rate of crystal growth in a solidifying mass is isotropic, the treatment above may be further advanced. This assumption is justifiable for pure aluminium and alloys containing little silicon, although it is less so when there is a pronounced tendency to dendritic growth, as in alloys of higher silicon content.

Fig. 21(*a*) illustrates schematically the growth of three crystals from the nuclei *A*, *B*, *C*. Each concentric arc represents the position of the solid–liquid interface at successive stages during crystal formation. (The arbitrary division of the solidification process into stages during which equal quantities of solid are formed results in a series of concentric shells, the thicknesses of which decrease as the radii increase.) The two sections *ADB* and *AEB* in Fig. 21(*b*) show quantitatively the variation in silicon content between two crystal nuclei, (i) in a straight line (*ADB*), and (ii) along a line passing through the point of latest solidification (*AEB*).

Fig. 21 shows that contact between adjacent crystals occurs before solidification is complete. A continuous solid network is therefore in

existence while intercrystalline spaces are still filled with liquid. Straining of such a mass would be expected to result in some plastic deformation, but failure would commence in the liquid regions and would result in a partly intercrystalline fracture. The typical transitional fractures encountered, particularly in the direct-casting test (see Section III), can be explained in this way. It would also be expected that straining at a temperature at which no adhesion between the

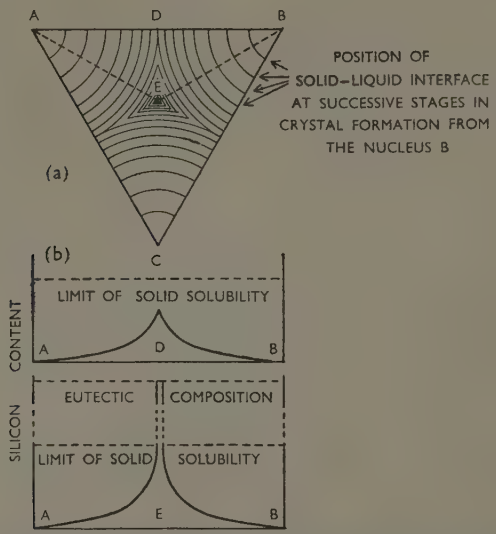


FIG. 21.—Schematic Representation of (*a*) Crystal Growth from Three Nuclei A, B, C, and (*b*) Distribution of Silicon Prior to Diffusion, in an Aluminium-Rich Aluminium–Silicon Alloy.

crystals had taken place would cause an entirely intercrystalline fracture, while straining in the complete absence of liquid (i.e. after total solidification) would result in a fracture of the ductile transcrystalline type. There should, from this reasoning, be signs of intercrystalline failure in all rapidly cooled alloys tested at temperatures above the eutectic temperature, since every rapidly solidified alloy must contain some eutectic at the crystal boundaries. In actual practice, wholly ductile fractures were obtained in the direct-casting test at temperatures considerably higher than the aluminium–silicon eutectic temperature in super-purity aluminium (which from the above reasoning might have

been expected to contain some eutectic), and in the 0·1 and 0·25% silicon alloys. This discrepancy may possibly be due either to the fact that small traces of liquid in the structure have a negligible effect on the mode of fracture, or to diffusion of silicon having caused a reduction in the silicon content at the crystal boundaries.

(b) *Effect of Reheating a Rapidly Solidified Alloy.*

In conditions which permit diffusion, as when a rapidly solidified alloy is reheated or maintained for some time at a high temperature, a flattening of the concentration gradients takes place within the mass. This affects every part of the alloy, but is greatest where the concentration gradients are steepest. By reference to Fig. 21 it is apparent that diffusion will be most pronounced at or near the crystal boundaries, and in alloys in which the eutectic layer at the boundaries is very thin, solution of this layer in the aluminium phase will be rapid compared with the effects of diffusion at points nearer the centres of the crystals. As soon as solution of the eutectic is complete at any point, further diffusion will result in a lowering of the silicon content of the solid solution, which will consequently become unsaturated: the temperature at which liquid formation takes place will then be raised. It may therefore be expected that an alloy of low silicon content tested at a temperature slightly above the eutectic temperature will, if tested in the rapidly solidified condition and in the absence of diffusion, fracture in an intercrystalline manner, but that if it is tested after sufficient time has been allowed for appreciable diffusion to occur, it may, at the same temperature of testing, be ductile.

The work of Jolivet and Armand [9] on the embrittlement of aluminium after casting is of particular interest in this connection. These workers observed that aluminium specimens of commercial and high purity, tested by means of a bend test at various temperatures during rapid cooling from the liquid state, were brittle at temperatures as low as 570° and 630° C., respectively. Slow cooling resulted in a raising from 570° to about 620° C. of the temperature at which ductile fractures were obtained in the metal of commercial purity, and the effect of reheating the material after rapid solidification was similarly to raise the temperature of embrittlement to about 620° C. The commercial-purity metal contained appreciable quantities of iron and silicon, and the low temperature of embrittlement obtained on rapid cooling was attributed by Jolivet and Armand to the formation of the ternary aluminium–iron–silicon eutectic, which freezes at 575° C. The elevation of the temperature of embrittlement during slow cooling or after reheating was

attributed to the formation of a eutectic of higher melting point, owing to diffusion and re-solution of the silicon present in even the high-purity aluminium.

As will be seen from the results recorded in Table II, the temperature of embrittlement was invariably higher in the reheated-casting tests than in the direct-casting tests. For two reasons, however, this result should be interpreted with some caution. Firstly, the respective test-pieces differed greatly in crystal size, so rendering any direct comparison of the results untrustworthy. Secondly, on the basis of the reasoning above, a difference in the temperature of embrittlement in the two tests would only be expected in certain alloys (namely those in which complete solution of eutectic is possible), whereas, in fact, the effect was observed in every alloy investigated. This latter feature of the results will be discussed later.

In order to eliminate the effect of crystal size, a series of direct-casting tests was made on super-purity aluminium in which testing was carried out, not after 2 min. but after 15 min. from the time of pouring. During this interval, the temperature of the cast specimen was maintained approximately constant at about 600° C., and was raised during the final four minutes so that the specimen was maintained for two minutes at the required temperature before testing. In these conditions, ductile fractures were found to occur at all temperatures up to and including 653° C., although no alteration in crystal size had occurred. The effect of the annealing had therefore been to raise the temperature of embrittlement by at least 20° C. The results of this experiment are illustrated by the dotted curve in Fig. 12.

The theoretical predictions were thus found to be borne out qualitatively in practice, but it is of value to consider the question further in order to determine whether the observed effect was, in fact, a result of the increase in the diffusion time brought about by the increase in the time between pouring and testing from 2 to 15 min.

Quantitative Treatment of Diffusion. Fig. 22(*a*) shows the silicon distribution near a crystal boundary in super-purity aluminium (which actually contains a trace of silicon), assuming that no diffusion occurs during solidification and that the rate of crystal growth is isotropic. The calculations upon which the Figure is based were made by the method of self-consistency mentioned previously. For the purpose of the present consideration, it is required to determine the time needed at a specified temperature for the silicon content at a point of maximum concentration to be reduced by diffusion to a lower level, this level, in the present discussion, being chosen as 0·1% silicon (the solidus temperature of an aluminium–0·1% silicon alloy that is wholly α solid solution is 653° C.).

The curve of silicon distribution in Fig. 22(*a*) is simplified in Fig. 22(*b*). In this latter Figure, the area under curve (1) equals the area enclosed by the curve in Fig. 22(*a*) between points where the silicon content is 0·1%. All points where the silicon content is less than 0·1% are considered to be outside the " hump ". Curve (2) encloses an equal

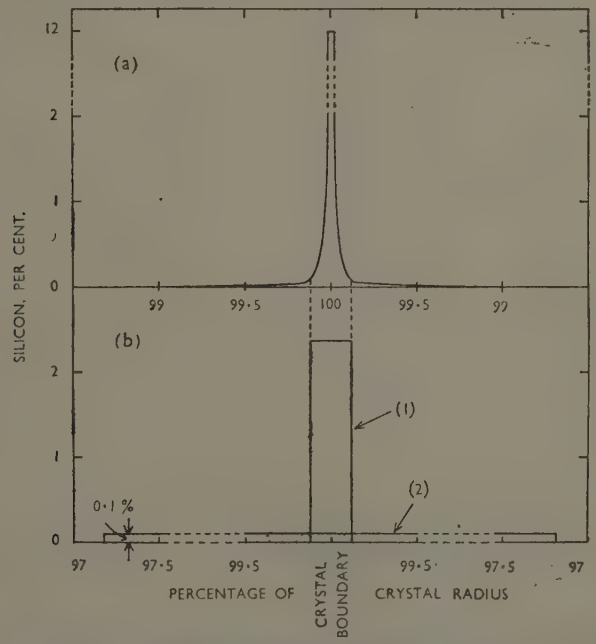


Fig. 22.—(*a*) Silicon Distribution Near a Crystal Boundary in Super-Purity Aluminium Prior to Diffusion. (*b*) Simplified Representation of the Silicon Distribution Near a Crystal Boundary in Super-Purity Aluminium (1) Before and (2) After Diffusion.

area, and represents the silicon distribution (simplified for purposes of calculation) after diffusion to the 0·1%-silicon level has taken place. It can be seen from the two curves in Fig. 22(*b*) that the average distance x traversed by a silicon atom during the diffusion is of the order of 1·4% of the crystal radius. From the examination of a number of suitable micro-sections, the average crystal radius was found to be about 0·2 cm., 1·4% of which is 0·0028 cm.

According to the kinetic theory, the time t required for linear

diffusion of an atom through any distance x is, to a first approximation, given by the following expression :

$$t \sim \frac{x^2}{2D} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where D is the diffusion coefficient at the temperature considered and is itself given by :

$$D = Ae^{-Q/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in equation (2), A and Q are constants which have been determined experimentally by Beerwald [10] for the diffusion of silicon in aluminium, R is the gas constant, and T the absolute temperature. At 600° C. D is found from equation (2) to equal $1{\cdot}94 \times 10^{-3}$ cm.^{2} day^{-1}. By introducing this figure and the known value of x in equation (1), the diffusion time t is found to be of the order of 3 min. Thus, at 600° C. diffusion of silicon away from the crystal boundaries until the concentration level falls to 0·1% silicon, takes place in minutes rather than seconds on the one hand or hours on the other. It thus seems that, on the basis of the diffusion of silicon, it is possible to explain the raising of the temperature of embrittlement which was observed in the extended tests with the direct-casting apparatus, and also the results obtained by Jolivet and Armand for commercial-purity aluminium.

(c) *Effect of Crystal Size.*

The dependence of the rate of diffusion on crystal size can be gauged from equation (1), in which the term x is directly proportional to the crystal diameter. Since the time required to reach a given stage in the diffusion process varies as the square of the crystal diameter, it is clear that a small alteration in crystal size will exert a large influence on the diffusion time.

The reason will now be apparent for the fact that the temperature of the ductile to brittle transition is higher in the reheated specimens than in those cast immediately before testing. In each case the time during which it was possible for diffusion to occur was of the same order of magnitude—approximately 30 sec.* and 120 sec. in the reheated- and direct-casting tests, respectively. The average diameter of the crystals in the reheated test-pieces was, however, smaller than in the directly-cast test-pieces by a factor of at least three (cf. Figs. 10 and 11, Plate XVIII), and diffusion would be expected to proceed at least nine times more rapidly in the former specimens than in the latter. For this reason, a

* In addition to the 20 sec. immersion of the reheated test-pieces in the lead bath before testing, some diffusion must have occurred during their original solidification. 30 sec. has hence been taken as the diffusion time.

nearer approach to equilibrium conditions would be expected in the reheated-casting test than in the direct-casting test.

It seems from the foregoing discussion that embrittlement at temperatures much lower than that of the equilibrium solidus in alloys containing up to about 0·5% silicon may well be caused by the presence of small amounts of liquid, since the existence of liquid at unusually low temperatures is readily explicable. There seems no reason, moreover, why this suggestion should not be true of alloys which contain more than 0·5% silicon. It was observed, however, that the point of embrittlement of all such alloys occurred at a temperature lower than the eutectic temperature. There are two possible causes for the existence of liquid in aluminium–silicon alloys at temperatures below that at which eutectic solidification is normally complete, namely (*a*) the occurrence of undercooling during the freezing of these alloys, and (*b*) the presence of traces of impurity, which introduce a ternary eutectic of lower melting point than the binary eutectic.

(d) *Effect of Undercooling.*

It is well known that aluminium–silicon alloys can readily be undercooled, and at any rate of cooling, other than the very slowest, the temperature at which maximum heat evolution occurs during the freezing of the eutectic alloy is lower than 577° C. Gayler [11] observed a depression of the eutectic temperature to 567° C. with rapid rates of cooling; and, according to Gwyer,[12] at any rate of cooling in excess of 15° C./min., the temperature at which maximum heat evolution occurs in the eutectic alloy remains constant at 561° C. This is approximately the temperature down to which the presence of liquid in the direct-casting test-pieces was suspected; and, on the basis of Gwyer's results, the rate of cooling in this test was compatible with this degree of undercooling. While it is thus possible to account for the low temperature of embrittlement encountered in the direct-casting test, the embrittlement of the reheated test-pieces (in alloys containing more than about 0·5% silicon) at approximately 571° C. cannot, of course, be ascribed to undercooling.

(e) *Effect of Impurities.*

An examination was made of specimens of the alloy containing 8% silicon, quenched in water from 575° and 572° C., in order to ascertain whether the quantities of liquid present in the alloy at these two temperatures were compatible with such liquid being a result of the formation of low-melting-point eutectics owing to the presence of impurities in the alloy. The areas of chilled liquid in the specimens

were clearly visible under the microscope, and, after quenching from 575° and 572° C., were of the order of 20% and 3% of the total area respectively. Clearly, the small traces of impurity present in the alloys (see Table I) could not have given rise to quantities of liquid of these magnitudes.

From this examination it was apparent that the formation of liquid in the alloy was not isothermal, but that liquid appeared in progressively greater amounts with increase in the specimen temperature from 571° to 577° C. The possible existence of temperature gradients within the specimens before quenching, which might have influenced the results, was not neglected, but such temperature gradients, if they existed, must have been small, since the liquid pools were evenly distributed across the sections of the specimens.

The transition from ductile to brittle fractures which occurred at 571° C. for reheated specimens of aluminium–silicon alloys containing more than about 0·5% silicon, is thus clearly associated with the formation of liquid in the alloys. The precise reason for the existence of liquid at such a temperature is, however, not clear, but in all probability it is due to a combination of the effects discussed above.

2. *Temperature of Non-Coherence.*

In many alloys, notably those possessing a wide freezing range, the characteristic properties of a solid, at least as regards coherence, are retained at temperatures well above the solidus. A sudden fall in strength, coupled with complete loss of ductility, occurs at or near the solidus temperature; but an appreciable strength persists on heating to higher temperatures, and it is not until the proportion of liquid is sufficient to destroy the coherence of the primary crystal network that the behaviour of the mass is that of a viscous liquid rather than that of a solid.

The temperature of non-coherence, as it may be termed, is less well defined than the temperature at which complete loss of ductility occurs. The strength–temperature curve tends to approach the temperature axis asymptotically, and the position of the point of non-coherence, as experimentally determined, depends on the sensitivity of the method used for its determination. It is of no advantage to compare the temperatures of non-coherence in the direct- and reheated-casting tests, because of the difference in the sensitivity of the two methods of testing. A true comparison can, however, be made between the temperatures at which the strengths of the alloys reach a certain level in the two tests. In choosing this arbitrary level it was realized that each alloy possessed a different inherent strength, and the level was therefore fixed for each

alloy at 2% of the strength of the alloy at a temperature immediately below the temperature of embrittlement. The "temperatures of 2% coherence" determined in this way are given in Table II, together with similar figures abstracted from the published curves of Singer and Cottrell.[4]

A direct comparison between the figures for 2% coherence is rendered somewhat difficult by the different degrees of approach to structural equilibrium of the same alloy when examined by the three methods of testing. This difficulty can be overcome by comparing the proportions of liquid present in the alloys at the temperature of 2% coherence in each condition of testing. The results of such calculations by the normal "tie-line" method, using the appropriate metastable constitutional diagram (see Figs. 23 and 24) and the corresponding diagram obtained by Singer and Cottrell, are given in Table II.

Two tendencies are apparent from the results:

(*a*) The proportion of liquid at the temperature of 2% coherence increases as the silicon content increases, up to about 0·5% silicon, and then approaches a steady value. (No figures are given for the high-silicon alloys, in which the influence of other factors renders the applicability of the tie-line rule questionable.)

(*b*) This steady value is different in all three tests, being 20–25% in the direct-casting test, 5% in the reheated-casting test, and 15–20% in the conditions of testing used by Singer and Cottrell.

When the liquid in a semi-solid mass is situated wholly between the crystals and is not entrapped between the dendrite arms, it is able to exert the maximum effect in lessening intercrystalline coherence; and the greater the proportion of liquid present in the crystal boundaries, the smaller the total amount of liquid in the mass necessary to cause a certain degree of lessening of coherence at any one temperature. From the results in Table II it would seem that when the liquid is situated wholly at the crystal boundaries, the proportion required to reduce the strength of the material to 2% of its value at the point of embrittlement is 5% of the total volume of the mass, or less. The factors which tend to cause entrapment of liquid between the dendrite arms are: (*a*) a pronounced dendritic structure—the dendritic structure is not pronounced in alloys of low silicon content, and thus, in these alloys, as is clear from Table II, liquid is more effective in reducing coherence because less of it is entrapped within the crystals; and (*b*) a large crystal size.[7]

The relation between crystal size and the proportion of liquid present at the temperature of 2% coherence is of interest. The proportion of liquid for 2% coherence was 20–25% in the direct-casting test-pieces in

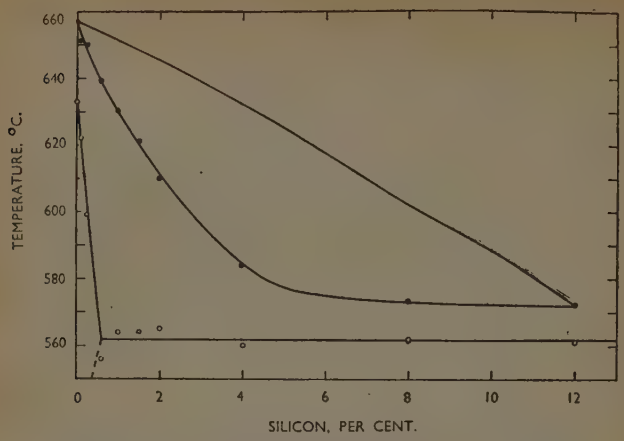


FIG. 23.—Suggested Constitution of Aluminium–Silicon Alloys in Conditions of Cooling.

●—● Temperature of 2% coherence.
○—○ Temperature of embrittlement.

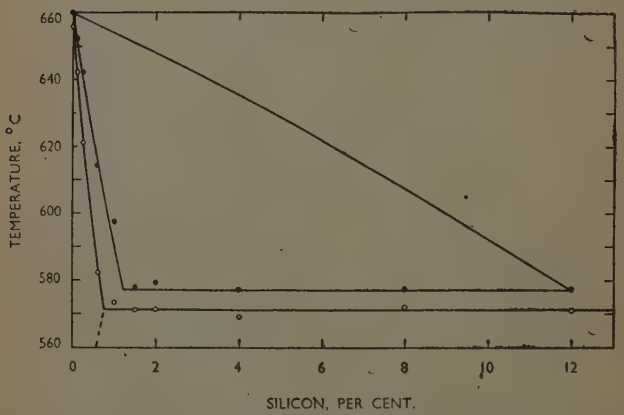


FIG. 24.—Suggested Constitution of Aluminium–Silicon Alloys in Conditions of Rapid Heating.

●—● Temperature of 2% coherence.
○—○ Temperature of embrittlement.

which the crystal size was large, and only 5% in the reheated test-pieces in which the crystal size was much finer. These figures suggest that the crystal size in the test-pieces used by Singer and Cottrell was intermediate and, if anything, rather large: the published photographs of their fractured test-pieces confirm that this was so.

It might be argued that the difference in the proportions of liquid present at the temperature of 2% coherence during heating from the solid state and cooling from the liquid state, is due, not to variations in crystal size, but to the fact that coherence is gained at a higher temperature during solidification than it is lost during melting; there seems, however, no reason for believing this to be so.

(a) *Critical Properties and Constitution.*

The temperatures of embrittlement and of 2% coherence are shown plotted against silicon content in Figs. 23 and 24, which refer to the direct-casting test and the reheated-casting test respectively. It is believed that these diagrams are closely related to the constitutional diagrams for aluminium–silicon alloys in the relevant conditions, in the same way as the corresponding diagram derived by Singer and Cottrell from the results of their high-temperature tensile tests was a close approximation to the constitutional diagram for equilibrium conditions.

The lower curves in Figs. 23 and 24 are drawn through the temperatures of embrittlement of the alloys in the conditions of the two tests. It has been shown that the temperature of embrittlement is probably the lowest temperature at which liquid exists in any alloy, and each curve therefore corresponds to the effective solidus of the constitutional diagram for the relevant conditions.

The curve drawn through the temperatures of 2% coherence has no constitutional significance, since alloys are of a duplex (liquid + solid) form both above and below it.

The liquidus curve, determined under conditions of continuous cooling on specimens in the direct-casting test, has been added to Fig. 23 in order to complete the diagram, although the determination of the liquidus curve did not form an important part of the present experimental work. This curve (the uppermost one in Fig. 23) is slightly lower than that determined in equilibrium conditions.

(b) *Application to Cracking at Temperatures in the Region of the Solidus.*

The results obtained in the present investigation can be directly related with the cracking of casting and welds in aluminium–silicon alloys at temperatures in the region of the solidus. Singer and Jennings[3] were able to correlate the tendency for cracking to occur in these alloys

with the brittle ranges of the alloys determined by Singer and Cottrell [4] in high-temperature tensile experiments. A more satisfactory correlation can be obtained by comparison with the brittle ranges determined during the course of the present work, in which the experimental conditions were much closer to those obtaining in casting and welding. The variation with silicon content of the extent of the brittle range (in the present instance the temperature range between the temperature of embrittlement and the temperature of 2% coherence), determined both

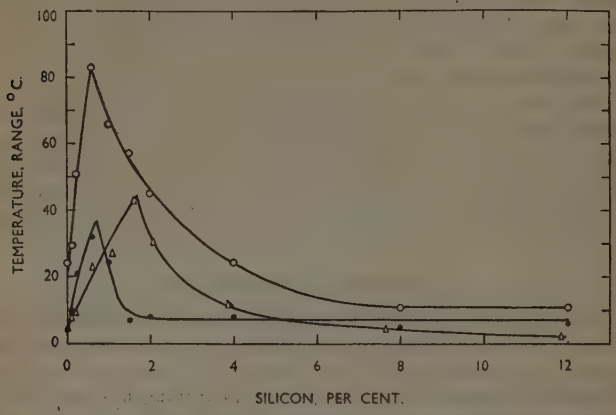


FIG. 25.—Brittle Ranges of Aluminium–Silicon Alloys in Three Different Conditions of Testing.

○—○ Direct-casting test.
●—● Reheated-casting test.
△—△ Results of tests by Singer and Cottrell.

from the present work and from that of Singer and Cottrell, is plotted in Fig. 25.

The curves relating to the present work show that the most extended brittle range occurs in an alloy of much lower silicon content than was the case in the investigation of Singer and Cottrell. A favourable comparison can be made between the silicon content corresponding to the maximum brittle range in the direct- and reheated-casting tests (0·6 and 0·7%) and the silicon content of the aluminium–silicon alloys giving maximum cracking in the ring-casting and restrained-weld tests (0·4 and 0·7%).

V.—Conclusions.

The results of high-temperature tensile tests on aluminium–silicon alloys, (*a*) in conditions of cooling from the liquid state and (*b*) after rapid reheating from the chill-cast state, show that in each condition of testing the strength–temperature curves in the region of the solidus are of essentially similar form to those determined in conditions of structural equilibrium.

The curves consist of: (*a*) a relatively low-temperature portion of moderate slope with respect to temperature, in which the alloys are characterized by their ductility, and (*b*) a high-temperature portion, normally of steeper slope but in many alloys becoming asymptotic to the temperature axis, in which the alloys behave as brittle materials.

The two temperatures of greatest interest on the strength–temperature curve are (1) the temperature corresponding to the discontinuity between the two component parts of the curve (the temperature of embrittlement), and (2) the temperature at which the strength falls to zero (the temperature of non-coherence), or in practice to a very low value.

1. *Temperature of Embrittlement.*

The assumption of Singer and Cottrell [4] that the temperature corresponding to the discontinuity in the strength–temperature curve was the solidus temperature, which was verified by them for aluminium–silicon alloys in conditions of structural equilibrium, has been upheld in the present work, in which it has been found possible to associate the temperature of the discontinuity fairly closely with the lowest temperature at which the alloys contain any liquid. In this connection, the following conclusions are of importance:

(*a*) Although the temperature above which an alloy behaves as a brittle material is normally the lowest temperature at which it contains liquid, very small traces of liquid may not cause true embrittlement. Thus, in alloys containing little of the solute element, the transition from brittle to ductile fractures as, during cooling, the temperature approaches the freezing point of the eutectic, is not sharp, and an intermediate type of fracture can occur in which plastic deformation and intercrystalline failure are both manifest.

(*b*) The concentration of the solute element within a rapidly formed crystal increases from the centre towards the outside. In a rapidly cooled alloy, subsequent diffusion is therefore most pronounced at and near the crystal boundaries, resulting—in eutectiferous alloys of low alloy content—in the early dispersal of traces of eutectic and the subse-

quent de-saturation of the solid solution. This has the effect of raising the temperature of incipient fusion, and hence displaces the discontinuity in the strength–temperature curve to a higher temperature. Such a displacement is, in practice, brought about whenever time is allowed for diffusion to occur, i.e. during slow solidification or remelting.

(*c*) Diffusion effects are particularly rapid in materials possessing a small crystal size, since the concentration gradients are steeper the smaller the size of the primary crystals. In aluminium containing a trace of silicon in which the crystal size is relatively large, appreciable diffusion of silicon away from the crystal boundaries can take place at 600° C. in a matter of minutes.

(*d*) Alloys tensile-tested during cooling from the liquid state may exhibit the discontinuity in the strength–temperature curve at a lower temperature than when tested after reheating, owing to the occurrence of undercooling. A difference in the discontinuity temperature of about 10° C. observed with aluminium–silicon alloys containing appreciable quantities of eutectic, has been attributed to this factor.

2. *Temperature of Non-Coherence.*

Although in any alloy, complete loss of strength during melting and gain of strength during solidification appear to be associated with the presence of a certain proportion of liquid in the mass, it is evident from the present work that this proportion of liquid varies considerably with the conditions of testing.

Further evidence has been obtained to support the suggestion of Singer and Cottrell that a relationship exists between the temperature range above the solidus in which an alloy gives a brittle fracture in a high-temperature tensile test and the tendency for that alloy to crack at high temperatures during casting and welding. As a result of tensile testing in conditions approximating to those which obtain during casting and welding, it has been found possible to associate the composition of the aluminium–silicon alloy possessing the greatest susceptibility to cracking during these processes, with that of the alloy in which the temperature range in which brittle fractures occur is most extended.

Acknowledgements.

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A CONSIDERATION OF THE NATURE OF BRITTLENESS AT TEMPERATURES ABOVE THE SOLIDUS IN CASTINGS AND WELDS IN ALUMINIUM ALLOYS.*

1153

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SYNOPSIS.

Previous papers have described the tendency of many aluminium alloys to crack at temperatures above the solidus during casting and welding operations. In the present paper, a critical examination is made of the cause of such cracking, and it is concluded that cracking of this nature occurs in the brittle temperature range, between the temperature at which a coherent dendrite structure is first developed in the alloy during cooling from the liquid state and the effective solidus temperature in the relevant conditions. The inherent tendency of an alloy to cracking at temperatures above the solidus is directly proportional to the extent of the brittle range and to the contraction that occurs during cooling through this range, and is independent of all external factors except those which alter the extent of the range.

The factors which affect the extent of the brittle temperature range are considered, and the relationship between the absolute tendency of an alloy to cracking at temperatures above the solidus and the results given by a test designed to observe such a tendency is discussed.

Finally, by way of example, a mathematical examination is made of the conditions which govern the occurrence of cracking in a butt weld between two parallel and restrained sheets of an aluminium alloy which possesses a wide freezing range and contains a small proportion of eutectic.

I.—INTRODUCTION.

THE tendency of certain aluminium alloys to a pronounced brittleness at high temperatures introduces many technological problems into such processes as pressing, forging, welding, and particularly casting. The reasons for this brittleness have not been generally understood, and although there may be a variety of causes for the appearance of cracks during the different processes, the term " hot-shortness " has, through general usage, become associated with brittleness at high temperatures wherever it occurs. " Hot-shortness " has also been used in a narrower sense to denote brittleness at temperatures above the effective solidus

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which is due to the presence of liquid films between the crystals of a semi-solid mass, and it is this phenomenon with which the present paper is concerned. In order to avoid confusion, however, the use of the somewhat unscientific term "hot-shortness" has been avoided as far as possible.

In an earlier paper [1] a theory was put forward relating the cracking of castings and welds in aluminium–silicon alloys with their constitution. This theory was based on the results of practical casting and welding tests and tensile tests of the alloys at high temperatures carried out by Singer and Cottrell.[2] Subsequent papers have described the cracking tendencies of many other aluminium alloys, and in these papers the original theory has been progressively extended with further experimental knowledge. It is felt that the time is now opportune for a complete statement of the theory in the light of existing knowledge on the subject, and an attempt has been made in the following discussion to clarify and to co-ordinate the ideas which have been advanced previously.

II.—The Cause of Cracking at Temperatures Above the Solidus.

The reason for the formation of cracks at temperatures above the solidus in certain materials during casting and welding may be understood by a consideration of the mechanism of solidification. Materials in which such cracking occurs invariably possess a freezing range, for it is found that pure metals and eutectic alloys are not susceptible to cracking at high temperatures. The solidification of an alloy of the solid-solution type provides a suitable basis for discussion.

During the cooling of such an alloy from the liquid state, the formation of primary dendrites commences at the liquidus temperature, and during subsequent cooling these dendrites grow at the expense of the liquid. While the proportion of liquid is still large, and the primary dendrites are not, in the main, in mutual contact, the pasty mass retains the properties of a viscous liquid; it has low strength, is able to flow, and the effects of surface tension are apparent. At a later stage in the cooling, however, the dendrites interlock and form a coherent network, the remaining liquid occupying the interstices. During the formation of this network there is a progressive increase in strength, and tensile experiments carried out at the appropriate temperatures show that the alloy gradually loses its power of flowing like a viscous liquid and exhibits the characteristics of a brittle solid. The material is incapable of appreciable extension, and fracture takes place by the formation of a rift in the network.

As the proportion of liquid falls, the strength of the alloy increases, but, while the dendrites are separated by a film of liquid, failure takes place at a stress lower than the strength of the individual crystals. These therefore undergo very little plastic deformation, and the brittleness persists until, with further cooling, the solidus temperature is reached. At this temperature the last traces of liquid freeze, and the material assumes its normal ductility.

It is clear that, under these conditions, the alloy is susceptible to cracking only while it is at a temperature in the brittle range, i.e. at a temperature between that at which it gains coherence and the solidus. Further proof of this point is provided by the fact that fractures produced in a tensile test carried out at a temperature in the brittle range closely resemble those which occur in castings and welds in alloys which crack readily at temperatures above the solidus. Cracking may be brought about by handling a casting or weld while part of it is in the brittle temperature range, but in general it is caused by the restraint of free contraction. The effect of this factor may be judged by considering a cast bar cooling from the liquid state under restraint at either end. If the bar is at the same temperature at all points, any cracking which occurs must be caused by the stresses due to the contraction of the network of primary crystals. In general, however, temperature gradients will exist along the length of the bar, and the cracking which takes place in the hottest parts is the result of the contraction of other parts of the bar which may be at temperatures below the solidus.

It is evident that the amount of contraction which occurs in a particular part of the bar while it is at a temperature in the brittle range determines the degree of cracking, and that the greater the contraction the more severe is the cracking. It is thus possible to define the inherent tendency to cracking of an alloy (as distinct from the amount of cracking or the number of cracks) as a function of the contraction taking place during cooling through the brittle range. Since such contraction may be restrained in three dimensions, it is reasonable to define this property as the shrinkage or volumetric contraction per unit volume during cooling through the brittle range. Thus the absolute tendency of a certain alloy to cracking is independent of all external factors except those (if any) which alter the extent of the brittle range. The relation between the tendency to cracking and the actual severity of cracking in particular circumstances depends on many factors, notably on the way in which the severity of cracking is measured. In addition, it will be apparent that the amount of cracking per unit length of the bar in the example above will be less when the temperature is uniform than it will be in the hottest parts when there

are temperature gradients along the bar. The effect of this latter condition clearly will be to increase the amount of cracking by a certain factor.

It is thus apparent why a certain alloy may exhibit widely differing degrees of cracking in different conditions. In the first instance, the extent of the brittle range is likely to be influenced by any factor which modifies the course of freezing, and this will, as a result, alter the inherent tendency to cracking. Secondly, the actual degree of cracking, while being related to the cracking tendency, is susceptible to the influence of external factors peculiar to the practical conditions.

III.—Terminology.

In order to avoid the use of cumbersome expressions, such as "the inherent tendency to cracking at temperatures above the solidus", which make a discussion of the subject unnecessarily lengthy, it will be of value at this stage to introduce and define a more convenient system of terminology.

(*a*) The term "hot-shortness", which has been used in previous papers to denote brittleness at temperatures above the solidus, but which also has a less restricted meaning, may conveniently be discarded. Cracking at lower temperatures is not considered in the present paper, and the phenomenon previously known as hot-shortness will therefore be referred to simply as brittleness, it being understood that such brittleness occurs only in the freezing range of an alloy.

(*b*) The volumetric contraction per unit volume during cooling through the brittle range will be called the brittle-shrinkage σ, and is given by:

$$\sigma = 3\alpha\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where α is the average coefficient of linear contraction over the solidification range and θ is the extent of the brittle temperature range, i.e. that range of temperature between the temperature at which coherence is gained and the solidus.

(*c*) The inherent tendency to cracking at temperatures above the solidus may now be referred to logically as the shrinkage-brittleness, since, as defined above, it is equal to the brittle-shrinkage. In referring to the susceptibility to cracking at temperatures above the solidus, the general term "brittleness" will henceforth be used less often than that which denotes the more particular property of shrinkage-brittleness. Clearly it would be desirable to include the idea of the presence of liquid in this term, but to do so is incompatible with succinctness.

(*d*) Many laboratory tests have been devised to provide an indication

of the shrinkage-brittleness of alloys. Such tests are frequently able to distinguish between two alloys of different shrinkage-brittleness, but they do not actually measure this property. Thus, for example, although the shrinkage-brittleness (or the brittle-shrinkage) has no dimensions since :

$$\sigma = 3\alpha\theta$$
$$= \frac{[L]}{[L]\,[\theta]} \cdot [\theta] = 1$$

laboratory tests may yield results expressed as the length of cracking in inches or they may serve to place an alloy in one of several categories. A distinction must therefore be made between the brittle-shrinkage and the result of a test, and the latter may be referred to as the rimosity. This word, to be precise, means the state of being fissured, but it is not in common metallurgical use and no confusion will be created by narrowing its meaning for the present purposes to signify the extent of fissuring.

It will be understood that rimosity is not a property which is susceptible of precise definition. It depends on the method of expressing the result of a test. When the test produces cracking to an extent dependent on the shrinkage-brittleness, the rimosity is the number of cracks or the length of cracking. When a series of tests of different severity is used, and the most severe conditions in which no cracking occurs is determined, the rimosity is the category in which an alloy can be placed as a result of the tests.

IV.—The Extent of the Brittle Range.

Since the brittle temperature range of an alloy lies within the freezing range, its extent is primarily dependent on the constitution. This is not to imply that other factors are insignificant, however ; as will be shown later their effects are very appreciable. The factors which have an affect on the extent of the brittle range may be considered under a number of separate headings :

1. *Constitutional Factors.*

The brittle range of an alloy extends from a temperature above the solidus at which there is a certain proportion of liquid in the mass down to the lowest temperature at which liquid is present. The limiting temperatures of the range are a function of the constitution of the alloy in the conditions of the experiment, and data obtained from the equilibrium diagram are therefore frequently unreliable. For example, in practical conditions of cooling, there may be a depression of the solidus and liquidus temperatures owing to the occurrence of undercooling, and

the effective position of the solidus may be still further lowered as a result of lack of diffusion.[3]

2. *Mode of Distribution of the Liquid Phase.*

The temperature at which a coherent network forms during the solidification of an alloy is dependent on the shape of the dendrites. If the dendrite arms are long and slender, they will make contact when the proportion of solid is lower than when they are short and thick. The temperature at which the last traces of liquid freeze will be the same in either case, so that the former type of dendritic growth is conducive to a longer brittle range than the latter.

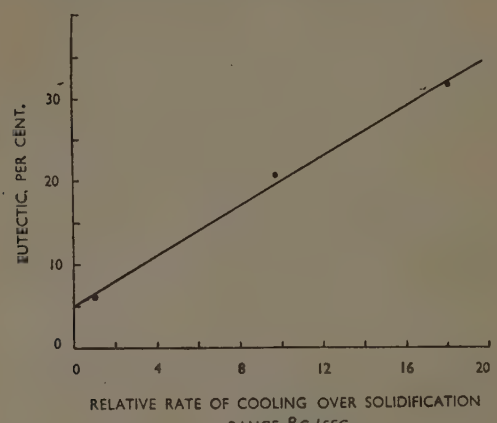


FIG. 1.—Relationship Between Rate of Cooling Over the Solidification Range and the Proportion of Eutectic Necessary to Prevent Cracking.

In a given alloy the form of the dendrites is dependent principally on the temperature gradients within the cooling mass, which are in turn determined by the rate of cooling. Some experiments were made with the ring-casting test devised in earlier work [1] to determine the effect of variation in the temperature of the cast-iron mould, into which the metal was cast and caused to solidify under restraint, on the cracking tendencies of a series of aluminium–silicon alloys. Increase in mould temperature caused a decrease in the rate of cooling of the solidifying castings, and the precise rates of cooling which obtained with different mould temperatures were measured by means of a D.C. amplifier and rapid-recording milli-ammeter. For each mould temperature used it

was found that additions of silicon to aluminium caused at first an increase in the rimosity, which reached a maximum at approximately 0·4% silicon with each mould temperature, although there was some tendency for the silicon content corresponding to maximum rimosity to be lower the higher the mould temperature, i.e. the slower the rate of cooling. Further increase in the silicon content above that corresponding to maximum rimosity resulted in a progressive reduction in cracking to zero value. The silicon content just sufficient to prevent cracking was smaller the slower the rate of cooling, and it was found that an approximately linear relationship existed between the proportion of eutectic in the alloy of the lowest silicon content which did not crack in a given set of circumstances and the average rate of cooling over the solidification range. This relationship is shown in Fig. 1. It will be seen that the most favourable conditions with regard to freedom from cracking would exist at an infinitely slow rate of cooling, and it is believed that the proportion of eutectic corresponding to this condition is indicative of the minimum proportion of liquid compatible with freedom from shrinkage-brittleness. Similar conditions appear to obtain with aluminium–copper alloys.

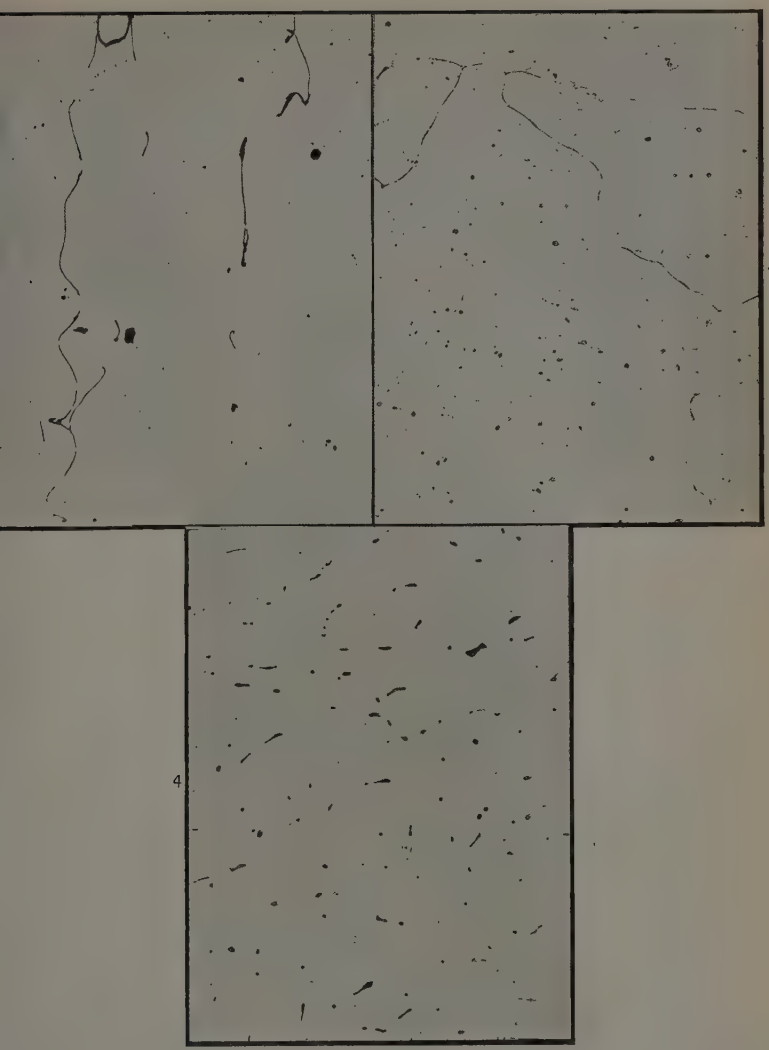
The mode of distribution of the eutectic liquid in the same alloy when cast into moulds at three different temperatures is illustrated in Figs. 2–4 (Plate XIX), which indicate the reason for the divergence in behaviour associated with the three corresponding cooling rates. The photomicrographs are of a 0·6% silicon alloy. Fig. 2 relates to a mould temperature of 500° C., and shows that at the rate of cooling associated with this condition nearly all the eutectic is situated at the crystal boundaries, which are clearly outlined. With a mould temperature of 300° C. (Fig. 3), a proportion of the eutectic is situated within the crystals, and the boundaries are less well marked; while with a mould temperature of 150° C. (Fig. 4), the crystal boundaries cannot be traced and all the eutectic appears to be located within the crystals.

It would thus appear that the slower the rate of cooling the higher is the proportion of eutectic liquid situated at the crystal boundaries, and that at very slow rates of cooling virtually all the eutectic is intercrystalline. The influence of the eutectic habit on the shrinkage-brittleness depends on the fact that the temperature at which a coherent network is formed in a solidifying metal mass is a function of the proportion of liquid between the dendrites, as opposed to the liquid between the arms of a single dendrite. If a dendrite grows in such a way as to entrap liquid within it, it will come into contact with adjacent dendrites at an earlier stage in the solidification process than when there is no entrapment, and the extent of the brittle range will be modified. A

minimum shrinkage-brittleness would be expected when there is no tendency for entrapment of liquid, and when, in consequence, all the eutectic in the finally solidified alloy is situated in the crystal boundaries. If it can be assumed that this optimum distribution of eutectic obtains when the cooling rate is very slow (as appears to be true from Figs. 2–4), the proportion of eutectic which corresponds with zero rimosity in the ring-casting test is shown by Fig. 1 to be of the order of 5%. This figure does not necessarily relate to zero shrinkage-brittleness, owing to the limitations of the test, and it will be apparent from a later Section that for zero shrinkage-brittleness to obtain, a slightly higher proportion of eutectic would be required.

This experimental observation leads to a more general conclusion, namely that during the solidification of an alloy, coherence is gained when the amount of *interdendritic* liquid (as distinct from liquid entrapped within the dendrites) falls below approximately 5%. In an alloy which freezes as a single solid solution there is, therefore, invariably a brittle range, but this is not necessarily true of a eutectic alloy. Such an alloy, provided that it contains 5% or more of interdendritic eutectic, will not gain coherence until the eutectic temperature is reached, and consequently will possess no brittle range. Hence the experimental observation that aluminium binary and ternary alloys show no tendency to cracking when the total alloy content exceeds a certain value.

It is of interest to compare the preceding conclusion with the results of tensile tests carried out on aluminium alloys at high temperatures. Such tests have shown [2, 3] that with aluminium–silicon alloys there is, for each alloy, a temperature at which coherence is gained, which is either between the liquidus and solidus, or coincident with the effective solidus in the relevant conditions. The precise temperatures of coherence are difficult to determine owing to the very gradual change in strength with alteration in temperature, but calculations have been made [3] of the proportion of liquid existing when the strength is 2% of the strength of the alloy when just solid. For each of the three methods of testing employed in the experimental work, namely testing in conditions of structural equilibrium and testing in metastable conditions during rapid heating from the solid state and rapid cooling from the liquid state, the figures were fairly constant throughout the series of alloys, but the results obtained in the different tests varied greatly. In one condition of testing it was found that appreciable coherence was gained when the alloy under test contained about 5% liquid, a result which is in agreement with the conclusion reached in the present paper. In another condition of testing the figure of 15–20% was obtained, but in this case it was observed that much of the liquid was " land-locked "



FIGS. 2–4.—Effect of Mould Temperature on the Eutectic Distribution in an Aluminium–Silicon Alloy Containing 0·6% Silicon. Etched in 0·5% aqueous HF solution. × 150.

FIG. 2.—Mould temperature 500° C.
FIG. 3.—Mould temperature 300° C.
FIG. 4.—Mould temperature 150° C.

[*To face p.* 242.

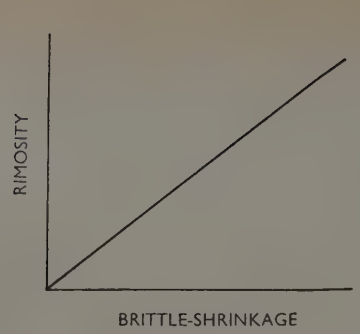
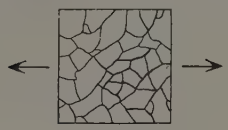


FIG. 5.—Relationship Between Brittle-Shrinkage and Rimosity for an Ideal Test.



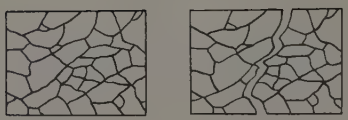


FIG. 6.—Schematic Representation of the Processes of (*b*) Accommodation and (*c*) Crack Formation.

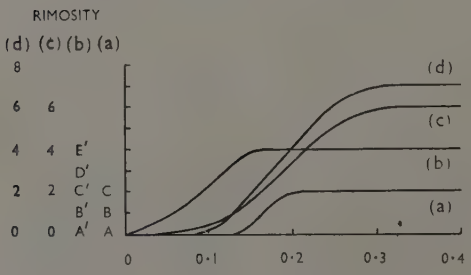


FIG. 7.—Relationship Between Brittle-Shrinkage and Rimosity for Four Practical Methods of Testing.

(*a*) Lees's test in sand moulds, category.
(*b*) Lees's test in copper dies, category.
(*c*) Restrained-weld test, length of cracking, inches.
(*d*) Ring-casting test, length of cracking, inches.

within the crystals, and the proportion of intercrystalline liquid may therefore have been more nearly equal to the figure of 5%.

3. *Factors which Influence the Mode of Distribution of Liquid.*

The casting experiments in which the temperature of the mould was varied showed that the shrinkage-brittleness of an alloy is dependent on the conditions which obtain during its solidification, i.e. on the rate of cooling. It was also observed previously [4] that a modification of the inherent shrinkage-brittleness in a number of the more common binary aluminium alloys could be effected in other ways, notably by alteration in the crystal size. More recent work has shown that small additions of titanium (which effect a reduction in the crystal size) to aluminium–silicon, aluminium–copper and aluminium–iron–silicon alloys, which normally crack badly, bring about a great improvement in this respect, and, within limits, the greater the reduction in the crystal size the more marked is the reduction in cracking.

These two experimental observations suggest that the degree to which liquid is entrapped between the dendrite arms during their formation is a function of the linear rate of crystal growth, i.e. that rate at which a dendrite arm advances into the surrounding liquid. It is possible to relate the rate of crystal growth with the two factors mentioned above, namely rate of cooling and crystal size. Thus a reduction in the rate of cooling increases the total time for solidification, and for a given crystal size the rate at which growth takes place from any one nucleus is, in consequence, lessened. If, however, the rate of cooling remains constant, an increase in the total number of nuclei in the cooling mass results in a reduced rate of growth for each one. Thus, decrease in either rate of cooling or crystal size, other things being constant, results in a decrease in the rate of crystal growth, that is, in a decrease in the rate of advancement of the dendrite arms into the surrounding liquid. The slower the rate of dendrite growth the greater is the tendency for liquid to be concentrated at the tips of the growing dendrites and the smaller the tendency for entrapment between the dendrite arms. Hence the experimental observation that with either a decrease in the rate of cooling or an increase in the number of nuclei in the cooling mass, i.e. a decrease in the crystal size, the greater is the proportion of liquid situated at the crystal boundaries of any alloy.

The chief factor which governs the dendrite formation, and hence the mode of distribution of the liquid in a solidifying alloy, is thus the linear rate of crystal growth. Such factors as (*a*) the effect of alloying additions on the dendrite configuration, and (*b*) the gas content of the alloy, are of secondary importance. The change in crystal size and shape

from a columnar to an equi-axed habit, which accompanies an increase in the percentage of alloying element, was noted in earlier papers. The presence of gas in a solidifying alloy appreciably reduces the shrinkage-brittleness, and according to Lees [5] the effect is most pronounced in alloys which contain a considerable proportion of eutectic. Lees attributes this behaviour to the pressure of the gas evolved during solidification of a casting causing eutectic liquid to flow into the hottest parts, where cracking is likely to occur. A similar effect may occur on a smaller scale, where the evolution of gas from the liquid situated between the arms of a dendrite may tend to force this liquid outwards and thereby increase the proportion of liquid at the crystal boundaries. In the absence of much detailed work on the effect of gas on shrinkage-brittleness, no experimental proof that such a process takes place has yet been furnished.

V.—The Relation Between Shrinkage-Brittleness and Rimosity.

The relation between the extent of the brittle range of an alloy and its shrinkage-brittleness has already been considered. As defined above, this relation is one of direct proportion (see equation (1)). Various tests have been devised with the primary object of enabling a distinction to be made between two or more alloys possessing different tendencies to cracking, rather than for measuring the absolute shrinkage-brittleness. Apart from the inability of such tests to provide any fundamental information, they possess the additional limitation of being applicable only to a certain range of shrinkage-brittleness. That is, they enable a differentiation to be made between two alloys provided that the shrinkage-brittleness of at least one of them lies within a certain range, but if neither lies within this range, both being either above or below it, the test will yield the same result for each alloy.

It is of value to consider the desirable attributes of an "ideal test". From the point of view of the usefulness of the result, as distinct from practical advantages such as the time required to perform the test, such a test should give a different result for every different value of brittle-shrinkage, that is, the rimosity should be proportional to the brittle-shrinkage. The characteristic curve relating brittle-shrinkage with rimosity for this test would be of the form shown in Fig. 5 (Plate XX). In this Figure it has been assumed that direct proportionality exists between rimosity and brittle-shrinkage, but this is not essential; the necessary requirement is that the curve should possess an appreciable slope for all values of brittle-shrinkage likely to be encountered.

Some knowledge of the maximum brittle-shrinkage attained in aluminium alloys is hence of importance. The most extended freezing range occurs in the aluminium–magnesium system, in certain alloys of which—in metastable conditions—it exceeds 200° C. The brittle range is thus seldom likely to be greatly in excess of 100° C., and in most aluminium alloys it will be considerably less. Assuming a volume coefficient of solid contraction of the order of 10^{-4},* it can be seen that the maximum value of the brittle-shrinkage is about 10^{-2}, or 1%.

It is now possible to compare the characteristic curves for some actual tests with that which would be given by an ideal test. Fig. 7 (Plate XX) shows the approximate forms of the brittle-shrinkage/rimosity curves for four tests, namely the ring-casting test, the restrained-weld test and the two tests used by Lees.[7] These curves have been constructed from experimental observations of the extent of the brittle temperature ranges in aluminium–silicon alloys,[3] together with data obtained in the work in which the four tests were used, and indicate the correspondence between the rimosity of a particular alloy as determined by each of the four tests. Three scales of rimosity have been used in the construction of the curves, owing to the different methods which have been employed for expressing the results of the tests. In the ring-casting and restrained-weld tests the length of cracking encountered is measured in inches, whereas in the tests in copper dies and sand moulds devised by Lees, each alloy is placed in a category depending on the severest conditions of testing under which it will not crack. For this reason, less importance should be attached to the absolute values of the slopes of the curves in Fig. 7 than to the forms of the curves. The curves are all of similar form and consist of a central portion over which there is a positive slope merging into a horizontal portion at either end. This form indicates that the sensitivity of the tests is a maximum over a certain range of brittle-shrinkage—which is different for each test—and decreases at either end of this range. Over the horizontal portion of the characteristic curve, a test is clearly incapable of differentiating between two alloys of different brittle-shrinkage.

It is of interest to compare the ranges of brittle-shrinkage over which each of the four tests may usefully be employed. The greatest power of differentiation is possessed by the restrained-weld test and the ring-casting test, the characteristic curves of which are very similar. These tests are sensitive up to a higher value of brittle-shrinkage than either

* Edwards [6] has reported that the coefficient of linear expansion of 99·95% aluminium between 500° and 600° C. is $33{\cdot}5 \times 10^{-6}$/° C., which corresponds to a volume coefficient of $1{\cdot}005 \times 10^{-4}$/° C. The values of the expansion coefficients of aluminium alloys are of the same order.

of the remaining two, but apparently not up to the maximum value, which may in some alloys be as high as 10^{-2} (1%). They are, however, at a disadvantage at the lower end of the scale since they are unable to provide any differentiation between alloys in which the brittle-shrinkage is less than about 10^{-3} (0·1%), and in this range the test in copper dies devised by Lees is of greater sensitivity.

It will be observed that a wider range of brittle-shrinkage values can be spanned by the use of both Lees's tests together than by the use of either alone, since the test in sand moulds becomes effective at approximately the point at which the copper-die test ceases to discriminate between alloys of different brittle-shrinkage. This was, in fact, indicated by Lees, who stated that each test was capable of discriminating between certain alloys which from the results of the other test would be grouped together as possessing the same susceptibility to hot-tearing.

VI.—Factors which Influence the Relation Between Shrinkage-Brittleness and Rimosity.

1. *Healing.*

In previous discussions of the cracking of aluminium alloys at temperatures above the solidus, much use has been made of the concept of "healing", whereby incipient cracks are considered to be filled with liquid and their ill-effects thus overcome. The occurrence of healing can in no way alter the brittle-shrinkage; it can be regarded as a separate effect from the tendency to cracking, and has the result of offsetting such a tendency. The concept of healing originated from the work of Verö,[8] who determined, by means of a casting test, the tendency of a series of aluminium–silicon alloys to cracking at high temperatures, and found that additions of up to 1·6% silicon to aluminium caused an increase in the severity of cracking. No cracking was encountered, however, in an alloy containing 1·88% silicon. Verö determined the strengths at temperatures above and slightly below the solidus of several alloys, including the 1·6 and 1·88% silicon alloys, but was unable to detect any essential difference in the form of the strength–temperature curves for these two alloys which might have accounted for the difference in their tendency to cracking. The explanation advanced to account for the difference was based on the fact that the 1·88% silicon alloy contained more eutectic than the 1·6% silicon alloy; and it was postulated that in a solidifying metal mass containing more than a certain critical proportion of eutectic, any cracks which were formed by the contraction of the primary crystals were healed by the inflow of eutectic liquid; from the results of the casting experiments it was suggested

that the critical proportion of liquid was 12–13%. Verö, however, did not provide any experimental evidence of the occurrence of healing.

A similar view of the healing process was taken by Lees,[7] who was able to discover an actual instance of its occurrence in an aluminium–copper alloy containing 4% copper, in which hot tearing had occurred because of the restraint of the free contraction of the solidifying metal by baked cores. In the instance reported, liquid had flowed in from a nearby feeder head and healed the tear. Lees did not explain how such healing liquid could be supplied in the absence of a convenient reservoir.

Singer and Jennings[1] found that in aluminium–silicon alloys, cracking occurred only when the silicon content was less than 3%, and concluded that the critical proportion of liquid was about 20%. They suggested that in the presence of more than this critical proportion, any cracks which formed at temperatures above the solidus were healed, but that cracks formed when the proportion of liquid was smaller were permanent. Singer and Jennings assumed the validity, in the conditions which obtained in their ring-casting tests, of the experimental observation of Singer and Cottrell,[2] that in conditions approaching structural equilibrium aluminium–silicon alloys retained coherency when up to 40% liquid was present in the mass, and postulated that during cooling between the temperature of coherence (that is, the temperature at which 40% of liquid was present) and the temperature at which the alloy contained 20% liquid, some relative movement of the crystals was possible without the formation of cracks. The degree to which an alloy is able to accommodate shrinkage stresses by slight movement of the crystals relative to one another within the semi-solid mass was thought to be a function of the proportion of liquid present, and it would seem that such accommodation can be identified with the previous concept of healing.

On the limited evidence advanced by Singer and Jennings there is no basis for believing that healing or accommodation can occur. It can be shown, however, that accommodation is a practical possibility. Fig. 7 (Plate XX) indicates that for three of the four tests for which a characteristic curve is given, the rimosity is zero when there is nevertheless a finite brittle-shrinkage; that is, alloys which possess a brittle range and which solidify in conditions of restraint do not always crack. It is difficult to imagine how this could occur without assuming accommodation to be possible. Although it is true that alloys which possess a brittle range do not always crack in the conditions of restraint obtaining in the ring-casting and restrained-weld tests, it may be objected that in Lees's[7] test in sand moulds various degrees of restraint were imposed, and the alloy might have been completely solid before

the restraining mechanism came into operation. Category *A* in Lees's tests corresponds with complete restraint, however, so that in this case the objection is not valid.

A consideration of the solidification of a butt weld also suggests that slight extension is possible when the alloy is at a temperature in the brittle range. In such conditions, an alloy containing a relatively high proportion of eutectic, and hence possessing no brittle temperature range, should have zero shrinkage-brittleness. It should, however, exhibit brittleness during the soldification of the last traces (5% or more) of liquid, because of the contraction of the parent metal. Such an alloy would therefore be expected to crack, and the fact that cracking does not invariably occur in such circumstances indicates a process of extension due to minor adjustments in the relative positions of the crystals.

It is therefore suggested that although accommodation is possible when an alloy is cooling through the brittle range, the healing of rifts in the primary network by the actual influx of liquid into them does not normally occur. The processes of accommodation and healing are easily confused, and Fig. 6 (Plate XX) illustrates, in diagrammatic form, the important difference between them. Fig. 6(*a*) represents the structure of the solidifying alloy prior to the imposition of the shrinkage or other stresses, and Fig. 6(*b*) the structure after accommodation of the imposed stresses has occurred by slight relative movement of the crystals, the attendant increase in length being accompanied by a decrease in width. When accommodation has proceeded as far as is possible, a rift may develop in the structure under the action of the applied stresses, as illustrated in Fig. 6(*c*). Any rift so formed may develop into a crack during further cooling, although it may be healed by flow of liquid into it when there is a high proportion of liquid present or when a particularly ready supply from another part of the mass is possible, as in the example given by Lees. Accommodation and healing can thus be regarded as separate phenomena which act to the same end ; that is, to reduce the amount of cracking obtained in an alloy in any practical circumstance. In welds and small castings, accommodation is more usual than healing, which necessitates the existence of a ready supply of liquid in one part of the mass (as in a feeder head for example) for the filling and healing of rifts formed in some adjacent part.

2. *The Distribution of Cracks.*

Cracks which form as a result of shrinkage-brittleness show considerable variation in size and shape, depending on the crystal structure of the material. A coarse crystal size favours the presence of a few

large cracks and a fine crystal size a larger number of smaller cracks. Subject to two reservations, however, the total volume of cracks which occur in any given alloy remains constant whatever the crystal size, the reservations being (1) that the extent of the brittle range may be affected by a change in crystal size, and (2) that accommodation, which results in a decrease in the total volume of cracks, may proceed to an extent which varies with the crystal size.

In a material of coarse crystal size any cracks will be plainly visible, but when the crystal size is small the value obtained for the rimosity may depend on the sensitivity of the method used in its measurement. Even if every crack were observed, however, a given rimosity in a material of large crystal size would not necessarily be equivalent in every respect to an equal rimosity in a fine structure, since the presence of a single crack affecting the whole section of a casting or weld is more serious in its effect on the mechanical properties than the presence of a large number of very small fissures. An interesting illustration of this effect was observed in certain aluminium–zinc alloys.[4] A weld in which the deposited weld metal possessed a coarse columnar structure, made in an alloy containing 20% zinc, was found to crack badly, whereas a casting of the same alloy, solidified in comparable conditions of restraint, in which the crystal size was fine, showed very little cracking. On examination under the microscope, it was observed that the casting contained numerous minute fissures, the length of each of which was of the same order as the crystal diameter.

3. *The Externally Applied Stress.*

Cracking in an alloy at temperatures above the solidus may be the result of two distinct mechanisms. Firstly, cracking may be due, as already discussed, to contraction of the dendrites with fall in temperature. In this instance, cracking is related to the conditions obtaining locally in the mass.

Secondly, cracking in a cooling mass is often brought about by externally applied stresses. Such stresses may be due either to incorrect handling of the casting or to temperature gradients within the mass. Handling a casting or weld while part of it is in the brittle temperature range may lead to the formation of cracks, the occurrence of which is well known to founders. The existence of temperature gradients results in the cooler parts of a solidifying mass escaping the effects of contraction. When the hottest parts reach the brittle range, the solid network is stressed as a result not only of its own contraction but also of that of the surrounding cooler material; i.e. the effect of the contraction of the whole is concentrated into the hottest (and weakest) parts. Locally,

therefore, the rimosity will be greater than the normal value, while elsewhere it will be zero, or considerably less than the normal value.

While temperature gradients exist in castings, they exist in a more pronounced form in welds, and the concentration of cracking in the hottest parts of the mass is, in consequence, more frequently observed in welds. Thus, for example, a butt weld between two sheets of an alloy which is brittle at high temperatures is often characterized by one long crack along the centre of the weld, at the junction line of the two sets of columnar crystals which grow into the weld pool from the parent sheets. There is, however, no evidence that the cracking of welds differs fundamentally from that of castings, although the precise mechanism by which cracking occurs is susceptible of considerable simplification in the case of welds, since, for the purposes of discussion, the phenomena can be considered to be confined to two dimensions instead of three.

VII.—Consideration of Weld Cracking.

Since dimensional simplification may be effected, it is possible to consider in some detail the conditions governing the occurrence of cracking in a straight butt weld between two parallel and restrained sheets of an alloy which possesses a wide freezing range and contains a small proportion of eutectic. In this consideration it will be assumed that the seam is long enough and that a sufficient length of weld has already been made for the thermal conditions to have become steady. The conditions then obtaining are illustrated in Fig. 8.

The two isotherms denote the positions of the liquidus and solidus, and the intervening area therefore consists of solid + liquid. To the left of the dotted line, heating is taking place, and to the right, cooling. The weld pool occupies the whole of the area bounded by the liquidus isotherm and extends slightly beyond into the duplex zone, to a distance determined by the temperature of coherence of the alloy. The duplex zone may thus be divided into two parts, the outer part being coherent and the inner ring consisting mainly of liquid with some solid. In the forward part of the weld, where the temperature is rising, this inner ring contains the remnants of the equi-axed crystals of the parent sheets which are suspended in the liquid. These crystals act as nuclei for crystal growth when the temperature commences to fall, those which happen to be suitably oriented forming the columnar crystals of the final solid weld.

The two sets of columnar crystals grow towards one another from the abutting parent plates at a rate determined initially by the temperature

gradient, but as the intervening gap narrows, their continued growth depends on the supply of liquid metal. In Fig. 8 those crystals to the left of the point *A* are growing freely, while those to the right are restricted in their growth. The point *A* may therefore be assumed to correspond approximately with the temperature of coherence, since it is found that at this temperature also liquid flow is hampered by the narrowness of the interdendritic channels. Certainly *A* is close to the liquidus isotherm since the tips of the columnar crystals must actually

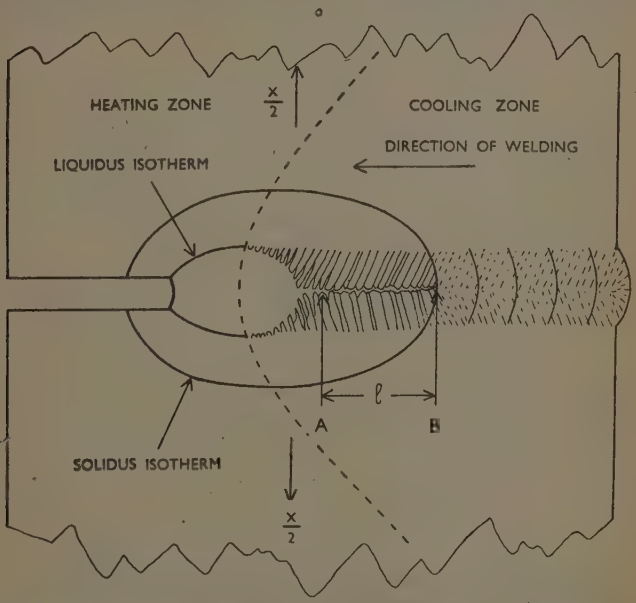


FIG. 8.—Conditions Obtaining in a Butt Weld Between Two Parallel and Restrained Metal Sheets.

extend to this line, and in the alloy considered the temperature of coherence is unlikely to be far removed from the liquidus, since the bulk of the solidification occurs just below this temperature. The area of restricted crystal growth extends to the point *B* on the solidus isotherm.

The supply of liquid metal past the point *A* on the line *AB* must be sufficient to compensate for solidification contraction and also for the increase in volume of the gap between *A* and *B* caused by the contraction of the parent sheets.

The rate of increase in width of the gap will be greatest at *A* and

progressively less towards B, owing to the restraining effect of the completed weld. Let the mean rate of increase be x.

Then, if the gap between the sheets is to be filled with metal when the weld has completely solidified, the volume V_s of solid metal deposited between A and B per second is given by:

$$V_s = xlb \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where l is the distance between A and B, and b is the mean thickness of the weld. If the corresponding volume of liquid metal is denoted by V_L, then:

$$V_L = xlb(1 + c) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where c is the solidification contraction.

Let the width of the gap at A be d. The whole of the liquid metal must flow through this gap along the channel AB, and because of the viscosity (η) of the metal, a certain pressure (P) will be required to actuate the flow. For a gap of constant width, and assuming that all the liquid flows the entire length of the channel, we may write:

$$V_L = \frac{Pd^3b}{8\eta l} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In actual practice, the quantity of liquid flowing past a certain point is dependent on the distance of that point from B, but the error introduced in this way is largely offset by the taper of the channel between A and B. Therefore:

$$\frac{Pd^3b}{8\eta l} = xlb(1 + c)$$

which reduces to:

$$P = \frac{8\eta l^2 x}{d^3}(1 + c) \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The necessary pressure P is derived from the existence of a liquid pressure lower than atmospheric in the channel AB, arising from the surface tension of the liquid metal, and the supply of liquid is therefore achieved by capillary flow. The maximum pressure difference which can be maintained by the surface of the liquid metal between the two sheets is equal to $\frac{2s}{d}$, where s is the surface tension.

1. *Condition for No Cracking.*

Cracking will take place when the pressure required to force the necessary quantity of liquid along the channel AB is greater than can

be supported by the surface film. The condition for the absence of cracking is therefore :

$$\frac{8\eta l^2 x}{d^3}(1 + c) \not> \frac{2s}{d}$$

which reduces to :

$$\frac{xl^2}{d^2} \not> \frac{s}{4\eta(1 + c)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The terms s, η, and c are constant for the limiting conditions considered, and equation (6) may therefore be rewritten as :

$$\frac{xl^2}{d^2} \not> k_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where k_1 is a constant.

2. *Rimosity.*

It may be assumed that the greater the amount by which $\frac{xl^2}{d^2}$ exceeds k_1, the worse will be the cracking, and to a first approximation, therefore, the rimosity R is given by :

$$R = k_2\left(\frac{xl^2}{d^2} - k_1\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where k_2 is a constant of proportionality. The terms x, l, and d depend on the particular conditions of welding, but they may be related to more fundamental quantities. Thus, x is proportional to α, the linear coefficient of expansion, and :

$$x = k_3\alpha \quad . \quad (9)$$

and l is dependent on the extent of the brittle temperature range θ.

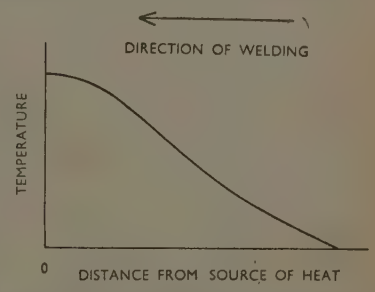


FIG. 9.—Variation of Temperature Along the Line of the Weld with Increasing Distance from the Source of Heat.

During welding, the temperature along the line of the weld decreases continuously with increasing distance from the source of heat, and the relation between l and θ depends on the form of the temperature–distance curve along the line AB. Owing to the high thermal conductivity of aluminium, the temperature gradients are less steep in the vicinity of the source of heat than they are further away, and at any one instant the temperature–distance curve along the line of the weld is of the form shown in Fig. 9. This curve is concave downwards in the vicinity of the source of heat and concave upwards at more remote locations. Assuming that points between A and B in Fig. 8 lie on the

former portion of the curve, then, to a first approximation, the relationship between l and θ can be expressed in the following way:

$$\theta = k_4 l^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and if this portion of the curve is parabolic in form:

$$\theta = k_4 l^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

From equation (1):

$$\sigma = 3\alpha\theta$$

where σ is the brittle shrinkage; and substituting for α and θ we have:

$$\sigma = k_5 \alpha l^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

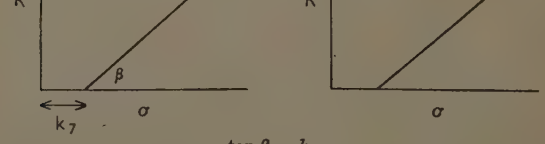
where k_5 is a constant equal to $\frac{3k_4}{k_3}$. Combining equations (8) and (12) the rimosity is given by:

$$R = k_2\left(\frac{\sigma}{k_5 d^2} - k_1\right) \quad . \quad . \quad . \quad . \quad . \quad (13)$$

in which the only unknown quantity is d. In the absence of experimental data, it is not possible to determine whether d is constant or variable. If d is a constant, equation (13) simplifies to:

$$R = k_6(\sigma - k_7) \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where $k_6 = \frac{k_2}{k_5 d^2}$ and $k_7 = k_1 \, . \, k_5 d^2$, and the relationship between R and σ is of the form shown in Fig. 10(a). In practice, the rimosity cannot exceed a certain maximum value (in the case of a weld, when the rimos-



$$\tan\beta = k_6$$

FIG. 10.—Theoretically Derived Relationship Between Brittle-Shrinkage (σ) and Rimosity (R).

ity is defined as the total length of cracking, $R_{max.}$ is determined by the length of the weld), and the relationship may therefore be modified as in Fig. 10(b). In view of the several assumptions made in its derivation, it is of interest to note that the theoretically constructed curve is of essentially the same form as the experimental relationship between brittle-shrinkage and rimosity shown in Fig. 7 (Plate XX).

Equation (14) also indicates that the rimosity is dependent on the extent of the brittle temperature range, for, since $\sigma = 3\alpha\theta$ and α is

approximately the same for most aluminium alloys (see footnote to p. 245), equation (14) may be rewritten as :

$$R = k_6(k_8\theta - k_7) \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Equation (8) indicates that the likelihood of cracking occurring in a weld is increased by increase in x or in l or by decrease in d. Increase in x can be effected by increase in the linear coefficient of expansion or by increase in the degree of restraint imposed on the sheets during the welding operation ; increase in l by increase in the brittle temperature range, the thermal conductivity, or the speed of welding. Increase in any of these quantities has been observed experimentally to increase the cracking obtained in butt welds. Decrease in d may be effected by increase in the linear rate of crystal growth, which in turn is increased by increase in the rate of cooling. Increase in this latter variable has been found by experiment to increase the tendency for cracking to occur. It would thus seem that equation (8) and its necessary corollary, equation (14), can serve to indicate the manner in which weld cracking will be affected by alteration in the physical properties of the material being welded or by modification of the welding technique.

VIII.—Conclusions.

(1) Cracking in aluminium alloys at temperatures above the solidus occurs in the brittle temperature range between the effective solidus temperature and the temperature at which a coherent dendrite structure is first formed in the alloy during cooling from the liquid state, and is a result of contraction stresses. The inherent tendency of an alloy to cracking at temperatures above the solidus (the shrinkage-brittleness) is directly proportional to the extent of the brittle range and to the contraction that occurs during cooling through this range, and is independent of all external factors except those which alter the extent of the brittle range.

(2) The extent of the brittle range is influenced by any factor which modifies the course of solidification. It is primarily determined by the constitution of the alloy in the relevant conditions, but it is also dependent on the amount and mode of distribution of the eutectic liquid within the mass. A minimum shrinkage-brittleness in any particular alloy is associated with conditions in which there is no tendency for entrapment of eutectic liquid between the growing dendrite arms during solidification, and when, in consequence, all the eutectic in the finally solidified alloy is situated at the crystal boundaries. The degree to which liquid is entrapped between the dendrite arms during their growth is a function of the linear rate of crystal growth, which in turn is principally dependent on such factors as rate of cooling and final crystal

size, although secondary factors such as the gas content of the alloy and the effect of alloying additions on the dendrite configuration are also of importance.

(3) The relation between the shrinkage-brittleness and the actual severity of cracking in particular circumstances (the rimosity) is dependent on a number of factors, notably on the way in which the severity of cracking is measured, and there is, for any test, a characteristic curve relating shrinkage-brittleness and rimosity, the precise form of which depends on the sensitivity of the test. The relationship between shrinkage-brittleness and rimosity may be modified in some measure if the alloy is capable of accommodating the contractional stresses in the brittle range by a process involving minor adjustments in the relative positions of the crystals. The rimosity is also dependent on the size and shape of the cracks which occur and on the external stresses to which the solidifying alloy is subjected.

(4) The conditions governing the occurrence of cracking in a straight butt weld between two parallel and restrained sheets of an aluminium alloy have been examined mathematically, and a relationship formulated which enables an estimate to be made of the manner in which weld cracking is likely to be affected by alteration in the physical properties of the material being welded or by a modification of the welding technique. In particular, this relationship indicates that the likelihood of cracking occurring in such conditions is increased by increase in the extent of the brittle temperature range, the speed of welding, the rate of cooling of the weld, the degree of restraint imposed on the sheets during the welding operation, the thermal conductivity, or the linear coefficient of thermal expansion of the material being welded.

Acknowledgements.

The authors wish to record their indebtedness to Professor L. Aitchison, D.Met., under whose general direction this work was carried out and to the Aluminium Development Association, which sanctioned the publication of this paper and whose members gave much generous assistance during the course of its preparation.

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A CONSIDERATION OF THE NATURE OF BRITTLENESS AT TEMPERATURES BELOW THE SOLIDUS IN CASTINGS AND WELDS IN ALUMINIUM ALLOYS.*

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SYNOPSIS.

Cracking during the casting and welding of aluminium alloys may occur at temperatures either above or considerably below the solidus. The nature of the former type of cracking has already been discussed in a previous paper (*J. Inst. Metals*, 1948–49, **75**, 235). In the present paper, cracking in aluminium alloys at temperatures below the solidus is considered, and it is concluded that the occurrence of such cracking depends on the ductility of the metal, on the conditions of stress to which a cooling metal is subjected at sub-solidus temperatures, and on the amount of cracking which occurs at temperatures above the solidus during the cooling of the metal from the liquid state. The likelihood of the appearance of sub-solidus cracking in industrial conditions of casting and welding, and possible methods for its avoidance, are discussed.

I.—INTRODUCTION.

MANY aluminium alloys are not readily weldable, mainly because of the cracks which occur in the weld metal or in the region of the weld either during or after completion of the welding operation. Cracking may occur at temperatures between the liquidus and solidus of the alloy considered, or at temperatures considerably below the solidus in castings and welds in certain alloys cooling under severe restraint. Although the second type of cracking is less common than the first, cracks observed at room temperatures in welded structures or in solidified castings may hence be of two distinct types, and may have occurred in widely different thermal and structural conditions. Although the two types of cracking have previously been distinguished by Verö [1] and Lees,[2] the term " hot-shortness " has, in general, been used to denote brittleness in alloys, irrespective of the temperature ranges in which such brittleness occurs.[3] Alloys susceptible to cracking at temperatures above the solidus may not be susceptible to cracking below the solidus, and the

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converse may also be true; and since the two types of cracking are due to fundamentally different causes, it is of obvious importance to differentiate between them and to obtain some understanding of the nature of both types of cracking if sound castings and welds in aluminium alloys are ultimately to be produced.

In a previous paper [4] consideration was given to the existence of brittle ranges at high temperatures in aluminium alloys, and their effect on the cracking of castings and welds in such alloys at temperatures above the solidus. In the present paper a discussion is presented of the occurrence of cracking in aluminium alloys at temperatures considerably below the solidus.

II.—The Nature and Occurrence of Cracking at Temperatures Below the Solidus.

In order to avoid the use of cumbersome expressions, the term sub-solidus cracking will henceforth be used to denote cracking which occurs at any temperature below the effective solidus in the relevant conditions during the casting and welding of aluminium alloys. True sub-solidus cracking occurs with some violence across the section of a casting or along the length of the weld when the temperature of the metal is within the range 200°–400° C., during cooling from the liquid state. The surface appearance of a fracture which occurs at temperatures below the solidus is different from that which occurs above the solidus; and the fractured surface of the casting in Fig. 1 (Plate XXI), in which both types of cracking were manifest, shows the essential difference between the two types of fracture. That portion of the fracture which occurred above the solidus is of the same colour as the metal itself and has a bright appearance, while the portion completed below the solidus is much darker in colour than the metal and has a characteristic brittle appearance. Sub-solidus cracking also differs from cracking which occurs above the solidus in that, in the case of a weld complex, for example, it may occur at any point in the complex—at the centre of the weld, at the edge of the weld, or in the basis metal—where the local conditions of structure and stress are conducive to its appearance.

In the examination of cracking during the casting and welding of alloys in a total of some 14 binary, ternary, and quaternary aluminium alloy systems, sub-solidus cracking has been observed only in certain alloys in the systems Al–Cu–Mg, Al–Cu–Mg–Si, and Al–Zn–Mg. Lees [2] has also reported the occurrence of sub-solidus cracking in cast bars of Y alloy and an aluminium–magnesium alloy containing 33% magnesium, cooled from the liquid state under restraint.

Above the solidus.

Below the solidus.

FIG. 1.—Cracking at Temperatures Above and Below the Solidus in a Cast Aluminium–Zinc–Magnesium Alloy. × 1.

FIG. 2.—Appearance of Weld in Restrained-Weld Test. × $\frac{2}{3}$ (approx.).

[*To face p.* 258.

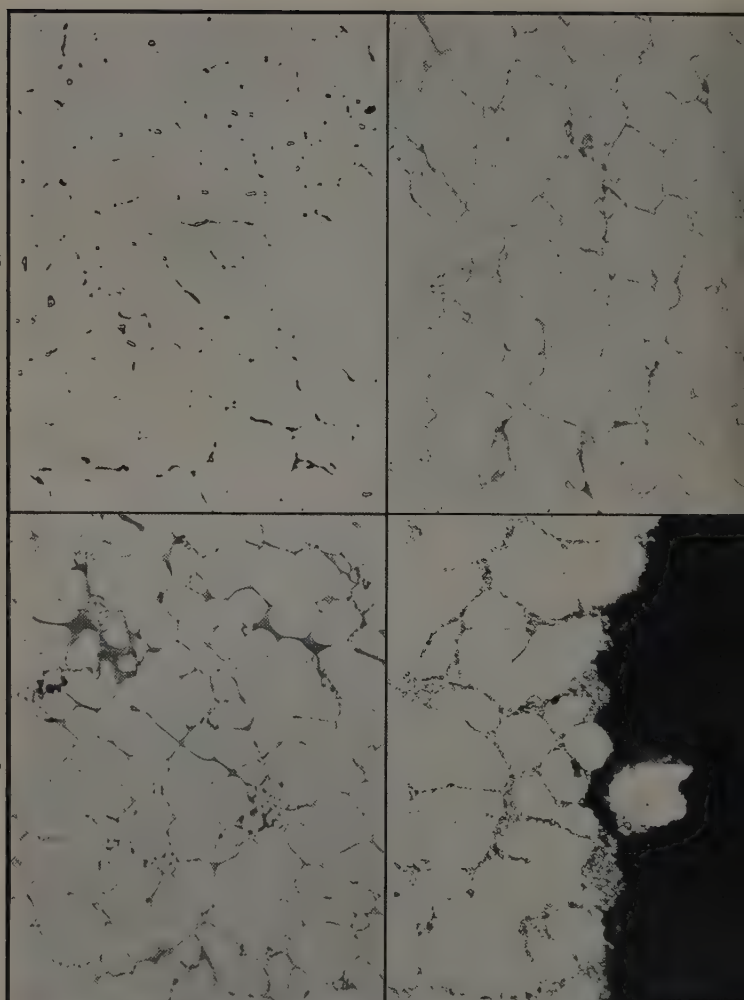

FIG. 3.—Weld in 1·0% Silicon + 1·0% Copper + 1·0% Magnesium Alloy. Etched in dil. H
× 200.

FIG. 4.—Weld in 1·0% Silicon + 3·0% Copper + 3% Magnesium Alloy. Etched in dil. H
× 200.

FIG. 5.—Weld in 1·0% Silicon + 4·0% Copper + 4·0% Magnesium Alloy. Etched in dil. H
× 200.

FIG. 6.—Fracture in Tensile-Test Specimen Taken from Weld in 6% Copper + 6% Magnesiu
Alloy. Etched in conc. HNO_3. × 500.

The amount of solid contraction which takes place in a casting or weld during cooling from the liquid state is dependent on the temperature range between the temperature at which the whole mass is first solid and room temperature. The effective solidus for the great majority of aluminium alloys of commercial importance is seldom less than 450° C. and in many instances is considerably higher. Hence, in cooling to room temperature (say 20° C.) an alloy will contract in the solid state over a minimum temperature range of 430° C. The coefficient of linear contraction over the range 450°–20° C. is, to a rough approximation, the same for all aluminium alloys, and is approximately 25×10^{-6}/° C. [5] Thus, assuming contraction is in no way restrained, a solid casting or weld in any aluminium alloy must contract in the solid state by at least 1% of its length in cooling to room temperature from the liquid state.

If contraction is in no way restrained, cracking cannot occur in any aluminium alloy at temperatures below the solidus. If contraction is totally restrained, then cracking will occur if the elongation of the material is less than 1%. Restraint of solid contraction in a cooling weld or casting may be brought about in a number of ways, particularly when the alloy being cast or welded is of low ductility. In a weld, the contraction of the weld metal may be restrained by the restraining effect of the metal at some distance from the weld, which has not become heated during the welding operation. Alternatively, contraction of the cooling weld may be opposed by an artificially imposed restraint, as in the restrained-weld test.[6] In a casting, solid contraction may be restrained by the effects of temperature gradients within the mass, which cause the contraction of the hotter regions to be opposed by the contraction of the surrounding cooler regions; contraction may also be restrained by contraction of the metal against a solid unyielding core.

Thus, in conditions of total restraint, cracking would be expected in a cooling metal mass at some temperature between the effective solidus and room temperature when the elongation of the alloy considered is less than 1% at that particular temperature. Since, at temperatures above about 225° C. the elongation properties of most commercial alloys increase markedly with increase in temperature,[5] cracking would not be expected to occur at temperatures much above 250° C., but would, in general, be expected to occur at 200° C. and below. Sub-solidus cracking in restrained welds in alloys in the Al–Cu–Mg and Al–Cu–Mg–Si systems and in cast bars of Y alloy [2] does, in general, occur at such temperatures.

There are, however, two anomalies which complicate the above simple conception of the problem. In the first instance, although

sub-solidus cracking may be observed in an alloy examined in the restrained-weld test, it is not invariable that cracking of this nature is observed in ring-casting tests of the same alloy; thus in 116 alloys in the Al–Cu–Mg and Al–Cu–Mg–Si systems examined by means of the ring-casting test, only 3 were observed to exhibit sub-solidus cracking, while of 23 alloys in these two systems examined by the restrained-weld test, 8 exhibited sub-solidus cracking. Secondly, sub-solidus cracking may occur in totally restrained welds in alloys in which the elongation at room temperature, and therefore at high temperatures, is considerably greater than 1%, as is evidenced by the results recorded in Table I.

TABLE I.—*Cracking in Aluminium Alloys Containing Copper, Magnesium, and Silicon.*

Nominal Composition.			Properties of Annealed Material.		Properties of Cast Material.		Cracking in Restrained-Weld Test.	
Cu, %.	Mg, %.	Si, %.	U.T.S., tons/in.²	Elongation,* %.	U.T.S., tons/in.²	Elongation,† %.	Above solidus, in.	Below solidus, in.
6·0	6·0	0	...	...	...	...	$0{\cdot}1_5$	6·5
1·0	1·0	0·5	9·1	20	...	...	9·2	0
2·0	2·0	0·5	10·6	8	...	...	6·8	0
3·0	3·0	0·5	9·0	7	...	...	$0{\cdot}4_5$	6·7
4·0	4·0	0·5	11·1	7	...	...	0	6·5
0·5	0·5	1·0	7·2	19	8·6	7	7·1	0
1·0	1·0	1·0	8·4	22	9·4	3	3·7	0
2·0	2·0	1·0	9·3	17	...	...	1·8	0
3·0	3·0	1·0	8·4	3	10·4	1	0·3	1·5
4·0	4·0	1·0	10·3	3	8·5	<1	0	6·5
1·0	1·0	2·0	8·4	23	...	...	$0{\cdot}2_5$	0
3·0	3·0	2·0	7·7	4	...	...	0	1·4
4·0	4·0	2·0	9·7	5	...	...	0	7·1
1·0	1·0	4·0	9·2	23	...	...	0	0
2·0	2·0	4·0	8·9	9	...	...	0	0

* % on 1 in. † % on 2 in.

Few, if any, aluminium alloys possess less than 1% elongation above room temperature, and hence, from the preceding remarks, sub-solidus cracking would not be expected to occur in any aluminium alloy, even in conditions in which the thermal contraction is totally restrained; and in fact, in alloys of high ductility, in which no, or very little, cracking occurs at temperatures above the solidus, no sub-solidus cracking is observed (see Table I). With alloys of relatively low ductility, however, in which some slight cracking occurs at temperatures above the solidus during cooling from the liquid state, the stress-raising effect of the cracks so formed may initiate cracking at temperatures consider-

ably below the solidus, if the thermal contraction is entirely restrained. When a considerable amount of cracking occurs at temperatures above the solidus, then, under conditions of complete restraint, as in the restrained-weld test, no sub-solidus cracking would be expected in even the least-ductile alloys, since the contraction stresses can be accommodated by the opening-out of the cracks already present in the section. This tendency is illustrated to some extent by the results in Table I. In the particular instance of the ring-casting test, the central cast-iron core is heated by the metal poured into the mould, and both core and ring cool together to room temperature. The coefficient of thermal contraction of cast iron is less than half that of any aluminium alloy, however, so that in these conditions there is some restraint imposed on the cooling ring; but, because of the contraction of the core, the restraint is only 50–60% of that which would obtain in conditions of total restraint. Thus, except in singular circumstances, sub-solidus cracking would not be expected during the cooling of a casting in the ring mould. The preceding general considerations are also applicable to cracking in welds. In the restrained-weld test, however, a central weld 3 in. in length is made between two sheets 4 in. wide, so that, after welding, the welded plate contains, in effect, a notch at either end of the weld run (see Fig. 2, Plate XXI). There is no appreciable contraction of the restraining jig after completion of the welding operation, and hence the contraction of the cooling metal is completely restrained.

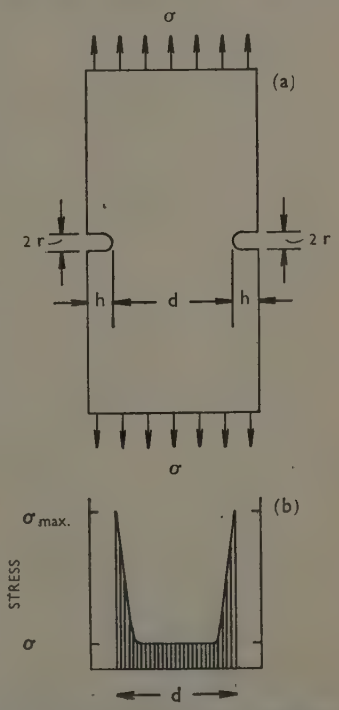

FIG. 7.—(*a*) Weld Complex with Notch at Either End of Weld. (*b*) Stress Distribution in Weld Complex Assuming Notches as in (*a*).

Singer and Jennings [6] found that in the absence of severe cracking at temperatures above the solidus, the stress on a restrained-weld complex,

cooled in the restraining jig, approximated to the proportional limit of the alloy under examination, and increased from about 2 tons/in.^{2} for pure aluminium to about 8 tons/in.^{2} for an alloy containing 12% silicon.

The weld complex in Fig. 2 can be approximated to a plate containing two grooves of depth h which have a circular shape at the bottom with a radius of curvature r (see Fig. 7(a)). If a direct tension is applied to either end of such a plate, then the ratio k of the maximum stress $\sigma_{max.}$ at the bottom of the grooves to the average stress σ in the minimum section d is a function of the ratios $\frac{r}{d}$ and $\frac{h}{r}$. In the conditions of the restrained-weld test the following approximate values obtain for h, r, and d: $h = 0{\cdot}5$ in., $r = 0{\cdot}015$ in., and $d = 3{\cdot}0$ in. From the data given by Timoshenko,[7] it can be calculated that under these conditions the stress at the bottom of the grooves is considerably greater than three times the stress at the ends of the plate. If it is assumed that the grooves are hyperbolic in form, then k can be determined theoretically.[8] In the conditions illustrated in Fig. 8:

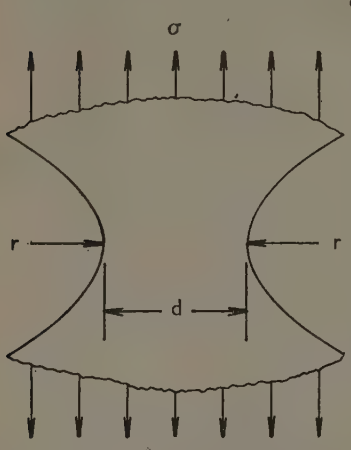

Fig. 8.—Weld Complex Assuming Hyperbolic Notches.

$$k = \sqrt{0{\cdot}8\,\frac{d}{r} + 1{\cdot}2} - 0{\cdot}1$$

For the restrained-weld test in these conditions, $k = 12{\cdot}5$ (approx.); that is, in the conditions envisaged in Fig. 8 the stress at the bottom of the grooves is more than 12 times as great as the average stress on the weld complex. It is difficult to estimate the value of k under the precise conditions of the restrained-weld test; in the stress-distribution diagram shown in Fig. 7(b), k has been assumed to have a value of 6.

As mentioned above, the stresses imposed on the weld complex in the restrained-weld test approximate to the proportional limit of the material; in such conditions, the stress distribution in the complex depends on the ductility of the material. With a ductile alloy the stress distribution beyond the yield point becomes more and more uniform as the material stretches, and there is hence no tendency for a " build-up "

of stress at the root of each notch. In the case of a brittle material, the high stress concentration at the root of each notch persists to the point of fracture. The average stress on the complex σ, and hence $\sigma_{max.}$, increases as the temperature decreases during cooling after the welding operation, and the precise temperature at which sudden failure occurs in a brittle alloy (i.e. the temperature at which $\sigma_{max.}$ exceeds the ultimate tensile strength of the material) depends on the degree of brittleness of the alloy.

In this connection, it is of interest to note that some sub-solidus cracking was observed in certain aluminium–zinc–magnesium alloys welded in the heat-treated condition, and not in the same alloys when welded in the annealed condition. The ductility of the basis sheet material was considerably less in the heat-treated than in the annealed condition.

At the completion of the welding operation in the restrained-weld test, when the metal at the finishing end of the weld is just solid, the temperature of the metal at the starting end is approximately 300° C. This initial uneven temperature distribution along the length of the weld causes an uneven stress distribution during cooling, which enhances the effect of the notch at the finishing point of the weld.

This consideration provides an explanation for the fact that with very brittle alloys sub-solidus cracking invariably commences at the root of the notch at the end of the welding run. In less brittle alloys, sub-solidus cracking may occur at other points in the weld complex or in the basis metal where, for any reason, the local conditions of stress are favourable for its initiation. Thus, if despite the notch effect, the cast material in the weld is stronger than the basis metal, fracture will tend to occur in the basis metal rather than in the weld, and the nature of such cracking as occurs, and its location relative to the weld bead, will depend on the ductility of the basis metal.

The occurrence of tri-axial stresses in the weld complex has been ignored in the discussion above, although it is realized that under such conditions of stress, a material which is normally considered to be reasonably ductile may fracture in a brittle manner with little elongation. This effect may further increase the tendency to sub-solidus cracking in welds in alloys which possess more than 1% elongation at room temperature.

III.—Factors Affecting Sub-Solidus Cracking.

It has already been mentioned that, in the complete absence of restraint of the thermal contraction, no sub-solidus cracking would be

expected to occur in either a casting or a weld during cooling from the liquid state, no matter how low the ductility of the material. In practical conditions of casting and welding, there is inevitably some restraint on the cooling metal, and whether sub-solidus cracking will occur or not depends on the degree of restraint and the ductility of the metal. The ductility of a metal depends on its structure; and, in general, the more complete the outlining of the crystal boundaries by a brittle intermetallic compound precipitated during cooling from the liquid state, the lower is the ductility of the metal and hence the greater the tendency for the occurrence of sub-solidus cracking. The structures shown in Figs. 3–5 (Plate XXII) are illustrative of this point. The structures are those of welds in three aluminium–copper–magnesium–silicon alloys tested in the restrained-weld test; the tendency to sub-solidus cracking increased markedly with increase in the amount of outlining phase from that shown in Fig. 3 to that shown in Fig. 5.

In order to confirm whether, in fact, fracture occurred preferentially at the crystal boundaries in the presence of an outlining phase, a tensile test was carried out [9] on a weld made without external restraint between two sheets of an aluminium–copper–magnesium alloy containing 6% copper and 6% magnesium. The results indicated that the alloy had practically no ductility, the elongation on a 2-in. gauge-length being of the order of 1–2%. Microscopic examination of the fracture indicated that fracture had occurred entirely at the crystal boundaries and that there was no distortion of the crystals in the region of the fracture. The appearance of the fracture is shown in Fig. 6 (Plate XXII).

In the systems in which sub-solidus cracking has been observed, the degree of outlining of the crystal boundaries with a brittle intermetallic compound increases with increase in the total alloy content. As has been shown,[4, 10] the tendency for alloys to crack at temperatures above the solidus during casting and welding decreases with increase in the total alloy content; and hence, alloys which because of their composition are least subject to cracking above the solidus, are most subject to sub-solidus cracking under severe conditions of stress. This effect is illustrated by the curves in Fig. 9, which show the ranges of composition in which the two types of cracking occur in welds in aluminium–copper–magnesium–silicon alloys containing 1% silicon and equal amounts of copper and magnesium. The shaded area in this Figure indicates the ranges of composition in which sub-solidus cracking occurs, the upper curve in this area representing the total amount of cracking in the alloys and the lower curve the amount of cracking which occurs at temperatures above the solidus. From a number of similar curves, complete ternary or quaternary diagrams can be constructed showing

the ranges of composition in which both types of cracking occur in any system.

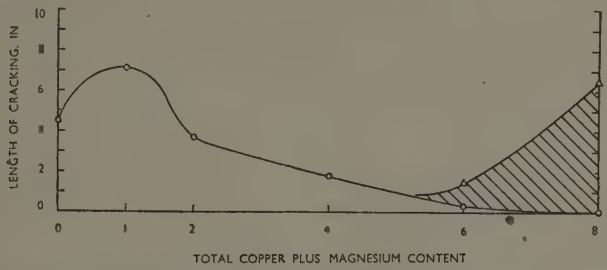

FIG. 9.—Cracking at Temperatures Above and Below the Solidus in Restrained Welds in Aluminium–Copper–Magnesium–Silicon Alloys Containing 1·0% Silicon and Equal Amounts of Copper and Magnesium.

○———○ Cracking above the solidus.
△———△ Cracking above and below the solidus.

IV.—The Occurrence of Sub-Solidus Cracking in Practical Conditions of Casting and Welding.

Although in the conditions of the restrained-weld test, cracking at temperatures considerably below the solidus is to be expected in all alloys of very low ductility when the restraint of solid contraction is not otherwise relieved, such cracking is unlikely to occur in practical conditions of casting and welding, since the restraint on the cooling metal in such conditions is, in general, considerably less than in the ring-casting and restrained-weld tests. Undue stress is avoided in industrial welding practice by careful design of the joints to be welded, and, in a complex component, by welding the several joints in a correct sequence. In addition, welding is almost invariably carried out on alloys in the wrought condition, in which case they are normally moderately ductile. Severe stresses are therefore unlikely to develop in industrially welded components during cooling after welding. With alloys of very low ductility, however, the presence of a notch effect at any point in the weld complex, owing either to incorrect design of the weld or to the occurrence of a slight amount of cracking above the solidus, may cause cracking at low temperatures. The welding of cast materials is rarely undertaken except in the repair of castings, and when such welding is to be carried out, the casting to be welded is normally pre-heated in order to avoid severe differential contractional stresses during, or after completion of, the welding operation.

In industrial conditions of casting there is unlikely to be any severe

external restraint of the solid contraction: firstly, because allowance is made for such solid contraction in pattern-making; secondly, because green-sand moulds are normally used for small and medium-sized aluminium castings, and such moulds will readily yield to accommodate solid contraction; and thirdly, because, in general, castings are knocked out of the moulds while still hot and before stresses of any magnitude have developed owing to the restraint of solid contraction by the mould and cores. Although external restraint of contraction is seldom encountered in industrial foundry practice, severe internal stresses may arise if the casting or billet is very large, in which case there will be severe differential contractional stresses across the section, owing to the outer layers of the mass cooling at a faster rate than the inner regions. Internal stresses may also arise if the casting is very complex and varies considerably in wall thickness so that differential cooling is pronounced, and at each reduction in wall thickness there is a severe notch effect. Under these conditions, sub-solidus cracking may occur in a casting or billet if the alloy of which the casting is made has negligible or low ductility. Sub-solidus cracking may also occur in such conditions in the presence of cracks formed above the solidus during the cooling of the mass from the liquid condition.

Whether or not cracking will occur at sub-solidus temperatures in castings or welds in industrial conditions depends therefore on the ductility of the metal (which is in turn dependent on its composition and structure), on the conditions of external and internal stress to which the cooling mass is subjected at sub-solidus temperatures (such stresses being determined by the design and size of the casting or weld complex), and on the amount of cracking which occurs at temperatures above the solidus during the cooling of the metal from the liquid state.

Sub-solidus cracking may consequently be avoided in industrial conditions by:

(1) Ensuring that the metal to be cast or welded has adequate ductility: in the case of many alloys ductility may be improved by adjustment of chemical composition or structure.

(2) Designing the casting or weld complex so that contraction of the metal during cooling is not unduly restrained and there are no undue stress-raising effects. In the case of large metal masses, differential contraction stresses may be reduced by slowly cooling the mass between the solidus and room temperature so that the temperature difference between outside and inside is reduced.

(3) Reducing the amount of cracking at temperatures above the solidus in the casting or weld by control of the several factors discussed in a previous paper.[4]

V.—Conclusions.

(1) Cracking at temperatures below the solidus has been observed in alloys in the systems Al–Cu–Mg, Al–Cu–Mg–Si, and Al–Zn–Mg, and by Lees [2] in Y alloy and an aluminium alloy containing 33% magnesium. The occurrence of such cracking depends on the ductility of the metal, on the conditions of external and internal stress to which a cooling metal is subjected at sub-solidus temperatures, and on the amount of cracking which occurs at temperatures above the solidus during the cooling of the metal from the liquid state.

(2) Alloys which crack at temperatures below the solidus in the restrained-weld test do not invariably so behave in the ring-casting test. The difference between the two tests has been ascribed to the pronounced stress-raising effect of the notch at either end of the weld bead in specimens tested in the restrained-weld test.

(3) It is not considered that sub-solidus cracking will normally be encountered in industrial conditions of casting and welding except where alloys of low ductility are exposed to severe contractional restraint. Sub-solidus cracking may, however, be encountered during the cooling of castings which are large in size or complex in form if the cast metal is of low ductility. In such instances, the degree of sub-solidus cracking which occurs may be regulated by control of the factors mentioned in (1) above.

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SOME METALLURGICAL PROBLEMS OF IMPORTANCE TO AIRCRAFT.* 1155

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Synopsis.

A brief review is given of some of the problems of aircraft construction in relation to design tendencies, materials available, and present difficulties.

The properties of modern light alloys of the aluminium-rich and magnesium-rich types are discussed and their suitability for aircraft applications considered. Reference is made to special characteristics of the aluminium–zinc–magnesium high-strength material and to recent advances in the use of magnesium-rich alloys.

Fatigue problems affecting aircraft structural materials are mentioned, and fields are indicated in which further work is required.

I.—Introduction.

All aircraft engineers profess a belief in the importance of low structure weight. The structure weight of an aircraft may for instance be 30%, and the civil or military load 15%, of the all-up weight. If, without sacrificing any durability or other properties, the structure weight could be reduced, for instance, to 29% and the pay load increased to 16% of the all-up weight, there would be an important improvement in the efficiency. Dr. Klein, consultant to Douglas Aircraft, has stated that the value of a saving of 1% of the all-up weight of a D.C.3 aircraft was comparable to the total initial cost of the aeroplane. Another authority gives the opinion that every pound of structural weight saved in the airframe or the engine for a passenger-carrying aircraft with a useful life of two years, is worth £30 sterling.

Recent tendencies in design are of importance in relation to the materials and their uses. One of the more notable features of the modern aircraft is a very smooth and regular external surface. The requirements vary somewhat according to the performance of the aircraft, and from place to place on the external surfaces. Not only must the latter be accurately true to form in respect of their general shape and remain so under the normal operational conditions, but they must have a very smooth finish. Tentative standards are that the height of chordwise waves must not exceed 0·001 in. on a length of 2 in. Spanwise waves may have about three times this height. Steps and local protuberances

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should not exceed 0·0005 in. These smooth wings are expected to have much reduced drag, which may be used either to give higher speed or lower fuel consumption. For aircraft of the future they will be needed on all types, from the high-speed fighter to the large transport. Another important trend is the use of thinner wing sections, demanded by aerodynamic considerations. This requires the use of spars of smaller depth, and generally makes less easy the attainment of the requisite strength and stiffness. On several modern aeroplanes, high-strength steel spar flanges are used on this account.

There is a general tendency to use thicker skinning than in the past. While sound from the point of view of strength and efficiency of the structure, this trend does not make the work of the constructor any the easier, owing to the greater difficulty of pre-forming thick sheets in strong alloys.

The present tendency to sweep back the wings to greater angles than have been customary in the past renders the design somewhat more complicated.

The sheets which form the external surfaces of an aircraft must be stabilized for resistance to rippling and local buckling. There are many ways of achieving this stability. The method of stabilizing by stringers is cumbersome, owing to the methods necessary for securing a good joint between sheet and stringer without producing irregularities in the form and smoothness of the external surface. Rivets in such positions have to be very nicely fitted, milled smooth afterwards, and any depressions filled up by some adhesive material to afford a smooth finish. Spot welding has made progress in this application. By the use of a flat electrode against the outer surface of the sheet, it has proved practicable to make satisfactory spot welds without seriously disturbing the smoothness of surface, but the welding conditions have to be carefully arranged to suit this particular condition. In addition, special jigging arrangements are required when the panels concerned are not flat. For the larger and fairly flat types of light-alloy panel, sheets having stringers integral in the same piece and protruding from the rear face of the panel, would appear likely to be very attractive if these could be produced by a rolling or extrusion technique, and there have been some attempts to produce such panels by machining from thick plates.

Much thought has been given to, and developments are in progress on, sandwich construction, i.e. two sheets of light alloy joined by a cellular structure of natural woods such as balsa, or a non-metallic foam, or treated paper. The mechanical characteristics required in the material for the filling are very moderate indeed, e.g. 10,000 lb. modulus,

density not greater than 6 lb./ft.^{3}, compression strength 100 lb./in.^{2}, and tensile strength 50 lb./in.^{2} On account of the sensitivity of glues and non-metallic materials to humidity and temperature, and their liability to set up corrosion of metallic parts, especially of light alloys, metallic foam or cellular material would be preferable.

For achieving local stiffness, a high Young's modulus and a high proof stress in tension and in compression in the materials of primary structure, are of importance. An improvement in Young's modulus of, say, 20% in an alloy of strength properties comparable to those of normal Duralumin would be of material advantage. Some interesting experiments on the possibility of increasing the Young's modulus of aluminium-rich alloys have been described by Dudzinski, Murray, Mott, and Chalmers.[1] The advantages likely to accrue from an increase in the elastic moduli of the aluminium alloys used in primary aircraft structures would be concerned with (*a*) the effect on characteristics that are a direct function of structural stiffness, i.e. on aero-elastic characteristics; (*b*) the effect on the natural frequencies of the aeroplane as an elastic system, which in turn determine the response, and hence the stress, in an aeroplane under dynamic loads; and (*c*) less weight for a given stiffness.

The full significance of ductility and elongation values is not yet clear. The properties of high-strength structural light alloys used in aircraft show, as would be expected, a sacrifice in ductility when tensile strength and proof stress are developed to high levels. Workability is, of course, required in all the materials of construction, and this alone places some limitation on the extent to which ductility can be sacrificed. The extent to which ductility assists in securing advantages by giving a more favourable distribution of load, e.g. in a riveted or spot-welded joint, is a matter to which a fair amount of attention is being given, especially under conditions of dynamic loading. Such effects in a structure may be superposed on intrinsic lower sensitivity to notch fatigue effect, e.g. at rivet holes that may be present, in one particular material as compared with another. Present information suggests that there may be limits below which the ductility cannot be reduced without loss of durability under fluctuating loads such as occur in service.

While resistance to tensile elastic deformation under a given load varies as Young's modulus $\times$ thickness, resistance to local wrinkling varies as modulus $\times$ thickness.[2] This means that lighter material has the advantage provided that $\frac{\text{modulus}}{\text{density}}$ remains the same.

Stability in compression is very important in aircraft work. The earlier magnesium-rich alloys were at some disadvantage, in that the

strength properties in compression were low, although the tensile properties were, in some cases, good.

The tendency towards thin wings throws a greater load on the skinning, which has to contribute more to the bending strength of the wing than in the earlier types of construction. High longitudinal and torsional stiffness are required. Wing-covering and spar-web materials of high modulus of rigidity would be of special advantage here. If means of stabilizing steel coverings could be devised, they might prove useful in aircraft of the future.

The major difficulties in designing an efficient structure are concerned with parts in compression. Whether the part is in the form of a strut or a plate, failure occurs by instability. For all such problems, leaving out the geometry of the part, the stress at failure depends on the tangent modulus. The form of the stress–strain curve in the high stress range is thus of great importance in design. It is usually considered that the 0·1% proof-stress values give a useful general indication of the merits of the materials.

From tests of strength of columns in compression, Van den Broek [2] concluded that material of the 75S-T type is definitely superior to all other metals tested in the short-column range, but that the magnesium-rich alloys compete for the award of merit in the long-column range, e.g. when l/k is of the order of >55 for aluminium alloy, and >44 for magnesium.

Extensive studies of the effects of cold working on light alloys of the aluminium-rich and magnesium-rich types in the U.S.A. and this country can hardly be dealt with adequately here, but a few general features may be worthy of mention. The laws of the effects of overstrain seem to be identical with those governing similar effects in mild steel. While internal stresses resulting from overstrain are probably not relieved at ageing temperatures commonly used in developing the full mechanical properties of light alloys, the Bauschinger effect (i.e. the increase in yield stress in tension by previous overstrain in tension, with reduction of yield stress in compression, or *vice versa*) is substantially removed by these low-temperature ageing treatments, e.g. in normal Duralumin by reheating to 120° C. for 16 hr. In general, for parts to withstand high stresses, cold working without subsequent heat-treatment at a low temperature to remove substantially the direction-consciousness of the material under working stress, is now thought by our leading experts to be deleterious to the general performance. In a few special cases, the properties of the overstrained material can be used to definite advantage. Cases in which sections are formed by transverse bending call for particular consideration in respect of these effects. The final

ageing treatments normally used on the strong (D.T.D. 546) and very strong (D.T.D. 687) sheet and strip seem, fortunately, to be of the kind giving the desired freedom from serious non-uniformity of stress–strain characteristics.

II.—Aluminium-Rich Alloys.

Aluminium alloys form the main materials of primary structure in modern aircraft, and usually account for more than half of the structure weight. A typical analysis of the structure weight of a large aircraft is 72·8% aluminium alloy sheet and sections, 7·2% steel, and 20% miscellaneous (including wheels, arches, shock absorbers, &c.) A good deal of the material in engines and equipment of civil and military types is also made of aluminium alloys.

For the highly stressed parts of British structures, extensive use is made of sheet and sections, basically of the modern D.T.D. 364 type of alloy, which contains, approximately, copper 3–4·5, magnesium $<0{\cdot}6$, manganese $<1{\cdot}2\%$, and small amounts of silicon, iron, &c. This material is used extensively for sheets, principally in "clad" forms, also for sections, tubes, and forgings. Several slight changes in this class of product since the cessation of hostilities have been concerned with a slight narrowing of the composition limits in order to permit greater standardization of heat-treatment temperatures without causing undesirable scatter of strength properties, and raising of the standard of purity of the aluminium cladding on clad sheets from 99·5% to 99·7% to secure high resistance to corrosion. In times of peace, longer life of aircraft is required, and the desire to avoid supplementary protective treatments or to cut down the thickness and weight of organic protective coatings to the minimum, demands high resistance to corrosion in the sheets used. Notable developments also are the production to closer limits of tolerance of dimensions and of flatness, and the manufacture of very large sheets for special panels. The subject of thickness tolerance for sheets is a very important one to the aircraft constructor, as well as to the manufacturer of the sheets. Russell [3] studied the thickness of sheets and found them to exceed nominal thickness by 7–7½%, although substantially within the limits of the current specification, with the result that the all-up weight of the aeroplane was increased by 1%, if the particular sheets examined were typical.

A leading development in the aluminium alloy field is the very high-strength type of alloy containing aluminium, zinc, magnesium, and usually a small amount of copper. Alloys of this class are coming into use for primary aircraft structures in the U.S. and the British aircraft industries.

Typical results of mechanical tests of a modern spar-boom extrusion, supplied to Specification D.T.D. 363A, of $1\frac{1}{4}$ in. thickness in the main section, are given in Table I.

TABLE I.

	Longitudinal Tension.*	Transverse Tension.*	Longitudinal Compression.	Transverse Compression.*
Proportionality limit, tons/in.^{2}	20·4, 26·6	26·6, 26·8	29·4	30·7, 30·7
0·1% proof stress, tons/in.^{2} .	36·4, 36·4	33·7, 33·4	37·4	37·3, 37·7
0·5% proof stress, tons/in.^{2} .	37·4, 37·2	35·6, 35·4	39·3	38·7, 39·8
Ultimate stress, tons/in.^{2} .	40·4, 40·5	38·1, 37·6	...	...
Elongation, % on $4\sqrt{A}$.	10·0, 9·0	8·0, 8·0	...	...
$E \times 10^{-6}$, lb./in.^{2} . . .	10·2, 10·1	10·1, 10·1	10·6	10·9, 11·1

* Results of duplicate tests are given.

The alloys contain approximately 5–8% zinc and 2–3·5% magnesium, with, usually, small amounts of copper, manganese, and chromium. They are heat-treatable, but the solution-treatment temperature used is somewhat lower than that for alloys of the Duralumin type. After quenching from the solution-treatment temperatures, age-hardening occurs at normal temperature, but more slowly than in Duralumin alloys, generally extending over several months. It is customary to develop high strength properties in these alloys by elevated-temperature ageing for a fairly long period at 120°–145° C., or by two ageing periods at slightly different temperatures for a total period of less duration than is customary when a single ageing treatment is used.

The alloys may be readily hot-worked. Stock for the usual hot-working processes is cast by the semi-continuous process, although very careful control is necessary for good results. The properties attainable in the alloys of this class are dependent, as indeed in other wrought alloys, on the history of the material in manufacture and on the finished form.

While the general corrosion-resistance of the alloys in the fully heat-treated condition is good, it is the general practice to use "clad" sheet and strip in aircraft applications. A pure aluminium coating is not suitable, and up to the present time a coating of high-grade aluminium containing about 1% zinc seems to be giving generally satisfactory results and to be preferable to other coatings that have been tried.

The main difficulties of the aircraft manufacturer in dealing with these very high-strength alloys are concerned with their working. Stiff members, such as spar booms, and also other forms are usually straightened in manufacture soon after solution heat-treatment, but many

FIG. 1.—Stretch-Forming End Sweeps from Flat D.T.D. 610A Strip in One Operation (Stretching).

[*To face p.* 271.

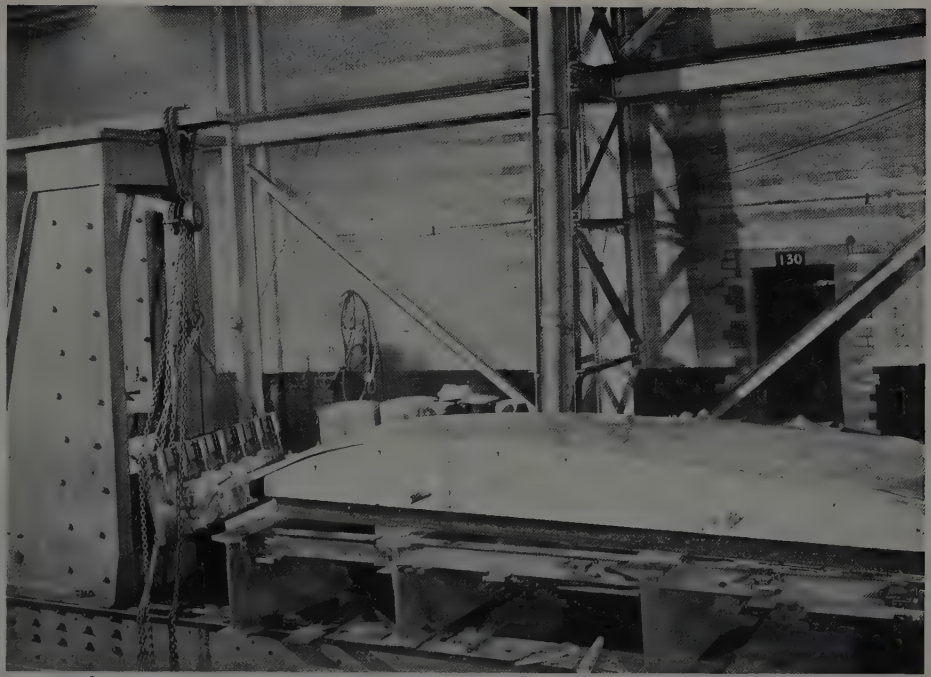

Fig. 2.—Stretch-Forming of Fuselage Double-Curvature Skin from Flat D.T.D. 610A Strip over Concrete Form Block.

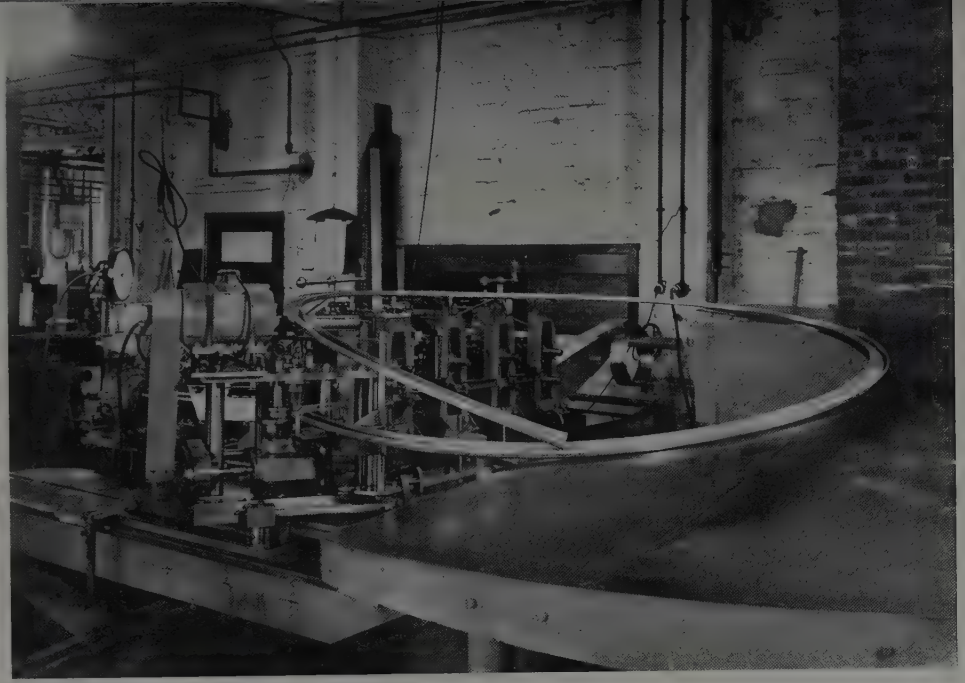

Fig. 3.—Producing Channel-Shaped Circular Formers from D.T.D. 610A Flat Strip in One Operation for Tudor II Fuselage.

FIG. 4.—Tank Access Door, Spot-Welded D.T.D. 390 (Lancaster).

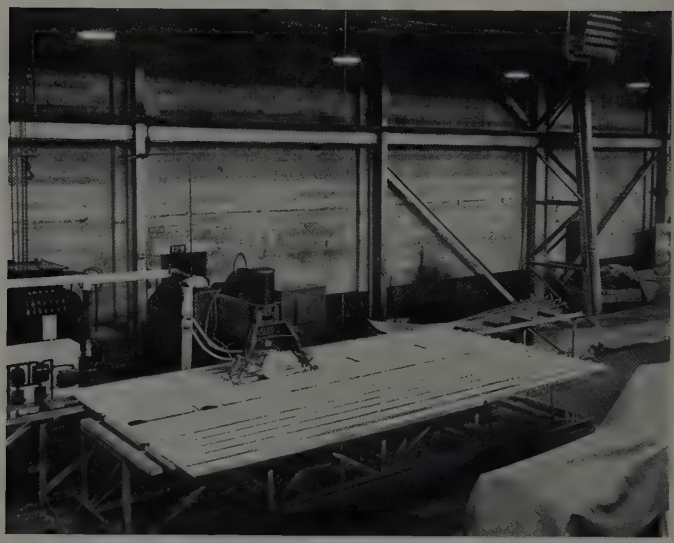

FIG. 5.—Roller-Welding Stringers on "Saddle-Back" Tank Skins. Material combination: 18 S.W.G.–18 S.W.G. D.T.D. 213; weld pitch: 1 in.

require to be "set" or formed in producing the actual aircraft components. Bending of a T, H, or angle section in the cold and in the high-strength condition must of necessity leave high internal stresses in the section, and these are disadvantageous from many points of view. Steps in the direction of manipulation at moderate temperatures, e.g. 170°–200° C., show promise of overcoming or alleviating some of these difficulties. In the United States, where developments in the use of these alloys in aircraft have been pursued vigorously, reheating to moderate temperatures before manipulation is in fairly general use.

Local pre-heating during dimpling of the sheets before riveting, has been utilized. The effect of these reheating operations is a function of time and temperature, but, with suitable control of temperature in particular, it would appear that there need only be a very moderate loss in strength properties, e.g. up to 5% of the static strength. In general, no other adverse effect of the over-ageing seems to have arisen, and the slightly over-aged condition appears, fortunately, not to be a dangerous one.

The constitution of ternary Al–Mg–Zn alloys has been investigated by Dix, Fink, and Willey,[4] and by Köster and Dullenkopf,[5] but the more recent work of Hume-Rothery, Raynor, Butchers, A. T. Little, K. Little, and Strawbridge[6] has added greatly to our knowledge of the constitution of the alloys and of the effects of additions of copper, manganese, and chromium. Further studies of the constitution of the alloys under the non-equilibrium conditions occurring in the products of industrial manufacture, and of the age-hardening phenomena in relation to the phases concerned, would seem likely to prove helpful to the better understanding of many of the properties of the alloys in question, and to their further development. Work on the Al–Mg–Zn wrought alloys in Germany followed quite a different course from that in other countries, probably owing to the different approach, the objective being at first to obtain an alloy having the strength properties of modern Duralumin but free from copper, which was in short supply in Germany for the armament-production programme. The alloy eventually selected for the aircraft industry contained approximately zinc 4·5, magnesium 3·5, manganese 0·3, and copper 0·4%, with small additions of chromium and vanadium. The alloy was heat-treated to give a minimum 0·2% proof stress of 25·6–26·7 tons/in.^{2}, and an ultimate tensile stress of 30·5–31·75 tons/in.^{2} in the fully heat-treated condition, according to the size and form of section, or to give lower values when in the normal-temperature-aged form. The alloy was used only to a very moderate extent, and in the later German aircraft

of the war period, for highly stressed components produced as sections or forgings, and only sparingly in sheet form.

The modern aircraft contains a good many sheet components made in light alloys of medium- and low-strength types, employed where stresses are not high or are easily carried by the sections that have to be used by reason of other considerations. Pressings, some of very deep profile, and spinnings have their particular uses, and the deep-drawing properties of sheet and strip alloys are of particular concern (see Figs. 1 and 2, Plates XXIII and XXIV).

The rubber press (Guérin) is used to form sheet components of fairly shallow profile on a very considerable scale. Stretch-forming to give single curvature or double curvature is also used effectively. Roll-forming is used for the manufacture of sections (Fig. 3, Plate XXV). These processes are used extensively on medium-strength alloys and on solution-treated unaged strong alloys.

As regards the airframe parts, joining of aluminium-rich alloys is principally effected by riveting. The rivets used are mainly of the well known types, Duralumin (L.37), low-copper alloy (D.T.D. 327), and 5% magnesium alloy (D.T.D. 303). The use of the very high-strength light alloys has raised the problem of rivets of appropriately high strength for use in these materials. Development work is in progress on very high-strength rivets and on " clad " rivets for high resistance to stress-corrosion. There seems to be scope for useful advances in this field.

Spot welding of light alloys is used extensively (Figs 4 and 5, Plate XXVI). The tendency is, as would be expected, to use spot welding where it can be applied conveniently and effectively. Spot-welded joints in the strong and very strong alloys, in general compare favourably with riveted joints as regards static strength, but under fluctuating stresses, riveted joints appear to give the better performance at the present stage of development of these two methods of making joints. As regards resistance to fluctuating stresses, joints of either kind in the very strong alloys appear at present to be no stronger than, or not as strong as, similar joints in the strong alloys, but our experience in this field is not very extensive, and studies of joint efficiency under static and dynamic loading conditions are likely to engage a good deal of attention in the next few years. In the aluminium alloy casting field, for highly stressed castings, the high-magnesium alloy (9·5–11·0% magnesium) D.T.D. 300, and the 4–5% copper alloys D.T.D. 298 and D.T.D. 304, are used extensively; a full range of alloys is used for miscellaneous sand- and die-castings for various applications.

III.—Magnesium-Rich Alloys.

The well known types of magnesium casting alloys are still used for a good many components, and forgings are also used to a considerable extent. Space does not permit a comprehensive account of the position of magnesium alloys in aircraft, but there are two important developments which should be mentioned.

The improved corrosion-resistance of magnesium and magnesium alloys containing only very small percentages of certain impurities, notably iron, copper, and nickel, brought to light by research work in the U.S.A. and in this country, has been confirmed by comprehensive investigations. The high-purity alloys of which there has been experience in this country, not only possess the advantage of high intrinsic resistance to corrosion but also prove to be very much more easily and effectively protected by the known methods of protecting magnesium alloys.

The preparation of high-purity alloys, even on a laboratory scale, demands the use of high-purity metals and the avoidance during melting and casting of contamination of the alloy. These features also apply to production on a commercial scale, but the manipulation is by no means so simple. The recent developments in this field, however, are in my view very promising indeed; and it seems probable that magnesium alloys having corrosion-resistance of the order of, or better than that of many aluminium alloys will be available in the fairly near future in cast and wrought forms. Specifications covering these alloys for aircraft applications have been recently issued. The main features are indicated in Table II.

While the types of alloy covered by these specifications are not materially different from commercial types in strength properties, they should be of particular value in aircraft applications. Full realization of the benefits that can be achieved as a result of their high purity will, however, necessitate appropriate treatments to ensure that an uncontaminated surface exists on the finished parts. Sand- or shot-blasting of castings is known to leave a surface which is very susceptible to corrosion, and there is scope for the development of a technique for subsequently removing the ill-effects of abrasive blasting treatments before the final surface finishes are applied. Surface purification is also very desirable on wrought products, the surface of which is liable to contain minute inclusions of foreign matter.

Another interesting and important development is that of the magnesium–zinc–zirconium alloys. British work in this field has been described by Ball [7] in his paper to the First International Magnesium

TABLE II.—*High-Purity Magnesium-Rich Alloys.*

Description.	Composition.									Mechanical Properties.			
	Main Elements.			Impurities.						0·1% proof stress, tons/in.²	Ultimate stress, tons/in.²	Elongation, %	Bend.
	Al, %.	Zn, %.	Mn, %.	Fe, %.	Si, %.	Cu, %.	Ni, %.	Sn, %.	Pb, %.				
High-purity magnesium alloy ingots	7·5–8·5	1·0	0·2–0·4	0·002	0·01	0·005	0·001	0·005	0·005	...	10	3	...
High-purity magnesium alloy castings D.T.D. 684	7·5–9·0	1·0	0·15–0·4	0·003	0·01	0·005	0·001	0·005	0·005	(4·5, information) (information—chill castings 4·5	14	8)	
High-purity magnesium alloy ingots (heat-treated)	7·5–8·5	1·0	0·2–0·4	0·002	0·01	0·005	0·001	0·005	0·005	...	14	6	...
High-purity magnesium alloy castings (heat-treated) D.T.D. 690	7·5–9·0	1·0	0·15–0·4	0·003	0·01	0·005	0·001	0·005	0·005	(4·5, information) (information—chill castings 4·5	15	10)	
High-purity magnesium alloy forgings and pressings D.T.D. 702	5·5–6·5	0·5–1·5	0·2–0·4	0·003	0·01	0·005	0·001	0·005	0·005	11	18	8	...
High-purity magnesium alloy sheets D.T.D. 707	8·0	3·0	0·15–2·0	0·003	0·01	0·005	0·001	0·005	0·005	10	18	12 *	6T † 4T ‡

* Sheets thicker than 12 S.W.G. † 180°: 12–15 S.W.G. ‡ 180°: 16 S.W.G. and thinner.

Congress. These alloys take advantage of the powerful grain-refining influence of zirconium and show very attractive mechanical properties, combined with very good working properties. The introduction of zirconium into the alloys has raised many problems, in connection with which Magnesium Elektron, Ltd., and their collaborators have done very good work. Specifications covering wrought forms of these alloys for aircraft applications have recently been issued, and the main features are indicated in Table III.

Production of these materials and of castings in similar alloys, in connection with which development work has already made good progress, necessitates the use of special techniques to ensure a suitable degree of dispersion of the zirconium in the melt and in the cast alloy, and reference should be made to the published papers for full details.[7] At their present stage of development, the alloys compare favourably as regards corrosion-resistance with other commercial magnesium-rich alloys; and it would be surprising if they did not show improvement, not only in corrosion-resistance but in mechanical properties, as further experience is gained.

Sand castings having quite attractive properties in the as-cast and in the heat-treated conditions are, it is understood, likely to be in full-scale production in the near future. It seems probable that castings having a 0·1% proof stress of about 8–8·5 tons/in.^{2}, an ultimate stress of 15·5–16·5 tons/in.^{2}, and an elongation of 8–10%, as cast, or a proof stress of about 9–10 tons/in.^{2}, an ultimate stress of 16–18 tons/in.^{2}, and an elongation of 7–9%, in the elevated-temperature-aged condition, will be attractive propositions for parts of aircraft and equipment.

Concurrently with these important advances, the cerium-bearing zirconium alloys have been the subject of very promising research and development work, some of the results of which have been described in a recent paper by Murphy and Payne.[8] These alloys are likely to find useful application in parts of engines which reach moderate temperatures in service.

The application of magnesium-rich alloys in primary structures has in the past been somewhat handicapped by the generally low or moderate tensile and compressive proof stress of these alloys, especially the latter, and the newer materials now becoming available seem likely to prove very much more useful. The advances in obtaining vastly increased corrosion-resistance by control of impurity levels will undoubtedly contribute to the more extensive use of the alloys.

There is a demand for abrasion-resistant protective coatings on magnesium alloys for a number of aircraft applications. Coatings affording a high degree of resistance to corrosion, and at the same time

TABLE III.—*Magnesium–Zinc–Zirconium Alloys.*

Description.	Composition.										Mechanical Properties.			
	Main Elements.					Impurities.						0·1% proof stress, tons/in.²	Ultimate stress, tons/in.²	Elongation, %	Bend.
	Al, %.	Zn, %.	Mn, %.	Cd, %.	Zr, %.	Fe, %.	Al, %.	Si, %.	Mn, %.	Cu, %.	Ni, %.				
Mg–Zn–Zr alloy forgings and pressings . . D.T.D. 619	...	1·0–7·0	...	...	0·5–1·0	0·01	0·02	0·01	0·15	0·03	0·005	13	19	8	...
Mg–Zn–Zr alloy bars and sections, medium strength, not greater than 3 in. . . D.T.D. 622	...	„	...	...	„	„	„	„	„	„	„	14	20	12	...
Mg–Zn–Zr alloy sheets. D.T.D. 626	...	„	...	...	„	„	„	„	„	„	„	11	17	8 *	4T †
Mg–Zn–Zr alloy bars and sections, medium strength, greater than 3 in. . . . D.T.D. 726	...	„	...	...	„	„	„	„	„	„	„	12	18	6	...
Mg–Zn–Zr alloy drop forgings . . . D.T.D. 729	...	„	...	...	„	„	„	„	„	„	„	11	17	8	...
Mg–Zn–Zr alloy extruded bars and sections, high strength, not greater than 3 in. D.T.D. 733	...	„	...	...	„	„	„	„	„	„	„	17	23	8	...
Mg–Zn–Zr alloy extruded bars and sections, high strength, greater than 3 in. . D.T.D. 744	...	„	...	...	„	„	„	„	„	„	„	14	20	8	...

possessing not only good adherence to the alloy base but intrinsic resistance to wear and tear, would be likely to prove very useful in aircraft work.

IV.—Fatigue Problems Connected with Aircraft.

Two important aspects of aircraft structural work are receiving a good deal of attention :

(*a*) the nature of the loads occurring in flight, and

(*b*) the behaviour and strength of aircraft structures under such loads.

There is a considerable amount of information available on fatigue properties of metals, as observed in laboratory tests of simple specimens. In the case of aluminium-rich alloys, it is well known that these materials do not generally show a definite fatigue limit, but that the S/N curves show a progressive fall, often very gradual at long endurances. In many cases no definite limit is attained at long endurances, e.g. of 500 million cycles. This seems to be an inherent characteristic of this important group of materials. The differences in form of the fatigue graphs for different alloys are at present unexplained. If more were known about these matters, perhaps the form of the graph could eventually be controlled. If the resistance to fatigue cracking at high endurances could be improved, so the performance of structures during long periods of service could be improved. Some of the more important magnesium-rich alloys show fatigue curves tending to a more definite fatigue limit.

The behaviour of these materials under fluctuating stresses is of importance also from the point of view of the influence of the mean tensile or compressive stress on the fatigue range. While strong aluminium-rich alloys tend to show only a slight reduction of range of alternating stress by mean tensile stresses of a moderate order, strong magnesium alloys are apparently more sensitive to the effect of mean tensile stresses. Determinations of the mean stress–fatigue range curves is extremely laborious work, involving very large numbers of specimens, since the determination of each single point necessitates breaking some six or eight fatigue specimens. A good deal of further work of this kind is required, not only on simple material tests, but also on specimens representing structural units.

Another feature of fatigue that is of particular interest in connection with aircraft, is the influence of rest periods. In the case of carbon steels there has been quite a considerable amount of evidence of benefit arising from periods of rest at normal temperatures. Daeves, Gerold,

and Schulz [9] found that rest periods after stress cycles exceeding the fatigue limit of 0·7–0·8%-carbon-steel wires resulted in increased endurance. The increase was the greater, in general, the smaller the number of stress cycles between the rest periods. Rest periods at temperatures somewhat higher than 50° C. showed more effect in increasing the endurance. Bollenrath and Cornelius [10] observed improved endurance of 0·02%-carbon soft iron after rest periods during fatigue tests; and Karius, Gerold, and Schulz [11] found that recovery in steel is greatest if the test is discontinued after 10–20% of the number of stress cycles that would be required to fracture the specimen. Bollenrath and Cornelius [10] looked for effects of rest periods in Duralumin and magnesium-rich alloys, but could not detect any influence. This field of study is one that is worthy of further attention.

Miner [12] has studied the cumulative damage in fatigue in light alloys. If N_1, N_2, N_3, &c., are the number of stress cycles of maximum stress S_1, S_2, S_3, &c., to produce failure, and if a smaller number of stress cycles, n_1, n_2, n_3 are applied in succession until failure eventually results, Miner derives the expression :

$$\frac{n_1}{N_1} + \frac{n_2}{N_2} + \frac{n_3}{N_3} + \cdots = 1$$

which embodies the concept of a cumulative effect of fatigue stressing. Miner's tests on light-alloy structural units showed fair agreement with values of $\frac{n_1}{N_1} + \frac{n_2}{N_2} \cdots$ of his expression. His test results he recorded as being in the range 0·61–1·49 for one series of experiments, and 0·98–1·05 for another.

While there is some other evidence to indicate that application of the lower-range stress cycles before the higher-range cycles increases the life of light-alloy structural units, the stress ranges on parts of an aircraft in flight are probably mixed at random, and it may well be that the net effect of the sequence is zero.

Gassner [13] has employed groups of load cycles, of magnitude and number corresponding to those observed in rectilinear flight, in the form of an integrated fatigue scheme.

Pugsley [14] has mentioned that in level flight there is a more or less continual occurrence of stress fluctuations of ±5 to ±10% about the mean, and suggests that the structure should remain airworthy during and after 5 repetitions of the proof load but should not break before 20 applications of that load. He further suggests that the structure should remain airworthy during and after 100 repetitions of loading to half the specified ultimate stress and should not collapse before 500 repetitions.

These considerations call attention to the importance of the behaviour of materials under stress cycles exceeding the stress ranges for long endurance. In recent years, a good deal of investigation work has been done on the subject of gusts. Lately, various factors have greatly increased the importance of gust effects in aircraft design. These are: increase in aeroplane speeds and decrease in the manœuvring load with increase in size. Each of these factors has contributed in raising the gust loads relatively until they have become, in many cases, the main design criteria for the flight structure. Loads due to a given gust vary linearly with the aeroplane speed. It is therefore safer to fly slowly in gusty weather. There is now a very considerable mass of information about the incidence of gusts in different geographical areas and at various altitudes. Analysis of gust data is enabling an assessment of the number and severity of the stress cycles superposed by gusts upon the mean stresses due to rectilinear flight. ' In this connection, the behaviour of structural units at mean stresses of from 0 to 50% of the ultimate failing load, and at superposed alternating stresses of up to about $\pm$ 40% of the ultimate failing load, is receiving close attention.

If simple methods of achieving joints in structures that would be more resistant to fatigue could be devised, they would be likely to be of great advantage in aircraft construction. Riveted, spot-welded, and glued joints in strong light alloys are all much weaker under fatigue stresses than the unjointed material. The resistance of joints to fatigue is an important problem.

V.—General Problems.

The aircraft of the future will fly higher than in the past, and in much colder conditions than have generally been encountered. Cabins and fuselages, and possibly other parts of aircraft, are being pressurized, and parts of them may have to operate under a very considerable steady stress, e.g. up to half the ultimate failing stress.

Leading edges are being heated for de-icing purposes, and parts of structures near to jet pipes are also subjected to raised temperatures. These uses of the materials of construction necessitate the employment of reliable data on the influence of long exposure to raised temperatures.

The modern gas-turbine engine is a concentration of metallurgical technique, embodying light alloys, corrosion- and heat-resisting steels, and high-temperature materials. These cannot be dealt with here, but that should not be taken as any indication of a lesser importance of that field of material studies, upon which the performance of the modern aircraft depends so closely.

ACKNOWLEDGEMENTS.

I should like to acknowledge gratefully my appreciation of the work done by my colleagues at Farnborough, Harefield, and Thames House, and elsewhere by the team of collaborators in the aircraft and aircraft-materials industries, and by research workers in various laboratories who are assisting on many of the problems I have mentioned. I should like also to thank the Chief Scientist, Ministry of Supply, for permission to present this paper. The assistance of Messrs. A. V. Roe in kindly providing a number of illustrations is also gratefully acknowledged.

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SYMPOSIUM ON METALLURGICAL ASPECTS OF NON-FERROUS METAL MELTING AND CASTING OF INGOTS FOR WORKING.

MELTING AND CASTING OF NON-FERROUS METALS.* 1156

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(Communication from the British Non-Ferrous Metals Research Association.)

Synopsis.

The requirements of good-quality castings for subsequent working are outlined by descriptions and illustrations of the more common defects in ingots, and the origin of these defects is discussed. In this connection, the solidification process of pure metals and of alloys freezing through a temperature range is described in some detail, and the main features of gas–metal equilibria are considered, including mention of sources of dissolved gases and the principles involved in methods of degassing.

The various commonly used casting methods are then reviewed, and attention is directed to those aspects of these processes which have an important bearing on ingot quality. Finally, present knowledge of the factors determining the structure of ingots is briefly surveyed, including reference to the features known to be important in working behaviour.

I.—Introduction.

This paper reviews the basic principles governing the production of good-quality non-ferrous metal ingots and billets for working. In the first place, it is assumed that the basic factors controlling quality in castings of this type are similar for the common industrial materials, although the relative importance of each may vary from one material to another. For example, divergences in the nature and properties of the oxide film formed on the liquid metal have widely varying influences on the behaviour of the metals in the melting and casting process, and although it is necessary here and there to refer to such differences of behaviour in different metals, the purpose of this paper is to discuss general principles rather than the individual idiosyncracies of specific materials. Such variations can better be brought out in later contributions to this symposium from those more intimately associated with production.

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This introductory paper, therefore, will deal in general terms with the requirements imposed by standards of quality, the ideal conditions of melting, pouring, and solidification, and the sequence of operations in the production of the casting, namely the preparation of the molten metal, the outstanding features of different casting methods, and the various factors involved in control of ingot quality. This contribution is primarily a review of available information and does not set out to report original work on the subject. While many references to published literature are given, no attempt has been made to prepare an exhaustive bibliography of so wide a subject.

II.—The Requirements of Good-Quality Cast Billets and Ingots.

The importance of a particular defect in a certain casting will depend on the subsequent working and service requirements of the material. Throughout much of this paper it is assumed that the objective is to produce a casting as free as possible from defects of any kind. Whether or not the attainment of perfection is economically possible has to be decided in the particular case, especially as the remedies for different defects are frequently not simultaneously applicable in commercial production.

1. *Surface Quality.*

The importance of surface quality among the requirements of a good casting is obviously determined to a large extent by the subsequent fabricating process. In some cases large surface defects may be eradicated by scalping at a relatively late stage in working, while in others small surface and sub-surface defects may have an important bearing on the quality of the final product.

The two most obvious types of surface defect encountered in production are folds in the ingot surface where the metal has in fact failed to fill the mould cavity completely, and inclusions of foreign matter in the skin of the ingot.[1]

Folds are of two types. The first is due to the presence of tenacious oxide films on the surface of the liquid metal which persist under the conditions of pouring and which wrinkle and fold like a crumpled sheet of paper, retaining the liquid metal within the wrinkled envelope and preventing it from conforming with the shape of the mould surface. Fig. 1 (Plate XXVII) illustrates this defect on the surface of a brass ingot. The second type is due to the rapid solidification of the extreme outer layer before the metal has had time to approach and lie closely against the mould face. Included in this type are splashes, where small

shots of metal thrown on the cold face of the mould solidify and are not remelted completely by the oncoming liquid surface, and cold shuts, particularly at sharp corners where heat extraction by the mould is most rapid.

Inclusions in the ingot surface arise primarily from oxide or slag poured into the mould from the crucible or melting furnace, or from particles of the mould coating becoming detached and embedded in the rising metal surface. The major offenders are relatively large particles floating on, and not wetted by, the molten material, and carbonaceous matter from the decomposition of volatile oil-base mould coatings.

The category of surface defects includes exudations of low-melting-point phases on the surfaces of the ingot. Such exudations can only occur after the bulk of the ingot is sufficiently rigid to allow contraction away from the mould face, leaving a gap between the ingot surface and the mould into which low-melting-point phases can exude. Such low-melting phases are generally much richer in alloying constituents than the average, and are usually brittle. They are undesirable, whether they form a smooth continuous skin or the more familiar rough and irregular patches. Fig. 2 (Plate XXVIII) shows tin sweat at the surface of a chill-cast bronze, and Fig. 3 (Plate XXVIII) shows how this brittle constituent breaks up on the surface of the rolled strip.

Finally, cracks in the ingot can be regarded as coming under the heading of surface quality, partly because they are most noticeable in the surface layers of the casting. Even if they are shallow and do not open further on subsequent working, they are liable to fold over during working and to result in flaws in the wrought product.

2. *Internal Soundness.*

Internal cavities in the cast metal may arise from the shrinkage in volume on passing from the liquid to the solid state, from gases given off from the liquid metal as it solidifies, or from gases carried into the interior of the casting during pouring and entrapped there by the solidifying metal.[1] Obviously, internal cavities resulting from any of these causes are inimical to the attainment of maximum properties. Their significance as a factor in ingot quality varies from one material to another, depending on the extent to which they impair the working behaviour of the material and the extent to which they persist in the finished product. Amounts of shrinkage porosity too small to affect working behaviour are unimportant in those cases where the cavities are eradicated by pressure welding during hot or cold working. It is theoretically possible to eradicate gas cavities in the same way if their surfaces are perfectly clean, and this is done every day in the production

of sheet from rimming steel ingots. When the cavity contains gas, however, pressure welding of the cavity surfaces must be preceded by diffusion of the gas into the adjoining metal, this being facilitated by the application of high pressure and high temperature. The extent to which this process occurs in non-ferrous metals appears to have received little attention, but it may safely be assumed that shrinkage cavities will be more easily eliminated in working than gas cavities, and to that extent are more tolerable in cast shapes for working. Sub-surface cavities arising from the injection and trapping of gas bubbles are particularly harmful to the surface quality of rolled sheet and strip, and Figs. 4 and 5 (Plate XXIX) illustrate the "spill" defect resulting from these cavities.

Other undesirable internal defects are non-metallic inclusions, suspended in the metal before pouring or formed on the metal surface during pouring and trapped in the casting. Non-metallic inclusions may be broken up during the working operation into small, relatively harmless particles, but in general they will have a mechanically-weakening effect on the metal to the extent to which they interrupt continuity; in this connection, oxide films formed on the pouring stream and carried into the mould may form deep-seated inclusions of a harmful type. Some types of non-metallic inclusions are, however, much more harmful than inert discontinuities would be. For example, in certain metals non-metallic phases may remain liquid after the metal is solid, and if the interfacial tensions between the liquid and solid phases satisfy certain conditions,[2] the liquid phase may spread over the surfaces of the crystals and thereby cause serious intercrystalline weakness. The behaviour of sulphur in this way in nickel alloys is well known and can have serious effects if not eliminated, whereas occasional isolated and inert sulphide particles in similar quantities in other materials can be practically innocuous.

3. *Structure.*

The structure to be aimed at is one capable of deformation in any direction with the minimum of effort and the greatest possible freedom from danger of cracking. This is generally achieved by the production of a uniform equi-axial grain, free from preferred orientations and large individual grains. Clearly, the desirable structure can only be defined in relation to the purity and constitution of the material. The alloy that necessarily consists of two phases should generally have those two phases as uniformly and as finely dispersed as possible, but hard and fast rules cannot be laid down without consideration of particular circumstances. For example, a coarse columnar macrostructure may be quite acceptable a pure isotropic metal or solid-solution-type alloy,

but the presence of minor impurities forming grain-boundary films of low melting point or ductility may make it imperative to refine the macrostructure and so minimize the grain-boundary weakness.

The term " inverse segregation " is often used to cover both the enrichment of the surface layers of the casting proper in the alloying element and the appearance on the surface of the casting of exudations of low-melting-point phases. The first of these, although significant in some cases, is relatively unimportant, but the exudations are usually very brittle and must be removed by machining.

4. *Internal Stresses.*

The presence of internal stresses can be a real problem in the production of castings of special shapes in either die- or sand-foundries. Internal stresses are less to be feared in the production of ingots and billets, where the dimensions and shape are such that restrictions on free contraction during cooling are rarely imposed. Clearly, if moulds are distorted, cracked, or otherwise shaped in such a way that free contraction of the casting is hindered, the casting will either crack or may well leave the foundry in a state of internal stress. Internal stresses in castings of this type arising from mechanical restraint by the mould are rare, and the possibility of the production of internal stresses by subsequent heat-treatment is outside the scope of the present paper. On the other hand, internal stresses arising from thermal causes present a serious problem [3] in some modern continuous and semi-continuous casting processes, where the ingot surface is drastically quenched by water sprays.

III.—The Solidification Process.

Before any attempt can be made to define the optimum conditions for the production of ingots for working, it will be necessary to consider just what happens when a metal solidifies; two types of material will be discussed, firstly the pure metal or the alloy solidifying at constant temperature, and secondly the alloy freezing over a temperature range. In the first instance it will be assumed that these materials are free from dissolved or mechanically entrapped gases.

In the solidification of a metal the major fact to bear in mind is that the change from the liquid to the solid state is accompanied by a volume change of the order of 3–7% (see Fig. 8). Such a change will result in cavities inside the ingot unless steps are taken to ensure that solidification only proceeds on a surface which is in contact with adequate supplies of reserve liquid metal. If this can be done, the reservoir of

feeding liquid will sink during the process of solidification, and the casting proper will be completely free from shrinkage defects.

In a pure metal this condition is met fairly easily because the metal forms a solid skin which advances inwards from the mould faces on a substantially plane front. Under ideal conditions, this front should advance from the bottom of the mould upwards, but, in fact, the heat is abstracted from the metal laterally, and the front, although relatively smooth, takes the form of a deep cup. If the depth of this cup is too great in relation to its cross-section, the solid faces advancing from opposite sides of the mould may bridge the gap and trap some of the

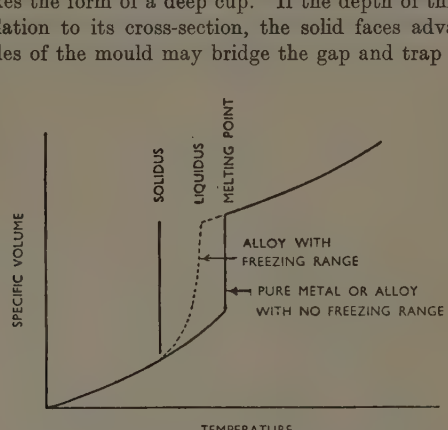


FIG. 8.—Specific Volume *versus* Temperature Curves.

The form of the curve between liquidus and solidus for an alloy with a freezing range depends mainly on the amount of metal solidifying at various temperatures in the range; in the case illustrated most of the metal separates in the upper third of the range and the specific-volume change in the lower two-thirds of the range is therefore relatively small.

liquid metal below the bridge. In this event, the freezing shrinkage of the liquid will produce a smooth-sided cavity at the heat centre of the isolated liquid.

A really pure metal is not liable to hot tearing, and if, for example, a mould cavity is larger in cross-section at the ends than at the middle, the contraction stress imposed on the metal in the mid-length of the bar will be relieved by plastic deformation. On the other hand, if there is a small amount of low-melting-point phase present, causing intercrystalline weakness over a certain range of temperature, cracks will form in such a casting near the middle of its length.

In an alloy with a freezing range, the solidification process is more complex, and the attainment of conditions giving maximum soundness

is correspondingly more difficult. The initial solid formed is deposited in a dendritic structure, in the interstices of which there exists liquid of lower melting point, and as the temperature falls, more and more of this liquid solidifies, filling the interdendritic spaces.

In the chill castings with which the present paper is concerned, there will generally be three well defined zones in the solidifying ingot, namely a wholly solid zone, a pasty zone between the solidus and liquidus isothermals, occupied by a mixture of solid and liquid metals, and a wholly liquid zone. In this case the freezing shrinkage occurring in the pasty zone is made up of two components, namely the freezing shrinkage of the liquid in the interdendritic spaces, and the solid shrinkage of the dendrites, which, of course, are cooling through the temperature range of freezing. Partly for this reason, the total bulk contraction in the pasty zone is generally higher than the freezing shrinkage of the basis metal, and this aggravates the already serious difficulty of ensuring an adequate flow of feeding liquid through the pasty zone. Clearly, if shrinkage cavities are to be avoided, liquid metal must be freely accessible to the metal in the pasty zone at the solidus interface, and this condition will only be met if the depth of the pasty zone is small, i.e. if the solidus and liquidus isothermals are brought close together. When this condition is attained, not only is the flow path of the feeding liquid relatively short, but also the interdendritic spaces are steeply tapered across the pasty zone, the ratio of their cross-sections to those of the solid metal being nil at the solidus isothermal and infinity at the liquidus. The distance across the pasty zone is clearly shorter the steeper the temperature gradients in that direction, and thus we arrive at the essential conditions for soundness in an alloy freezing over a wide temperature range, namely that solidification must not only occur in a direction towards the feeder head, as in a pure metal, but it must also occur rapidly. If this condition is not satisfied, small pools and films of residual liquid will become isolated in the interdendritic spaces, and their freezing shrinkage will produce relatively small convex-sided cavities, conforming in shape with the contours of the dendrites; in the extreme cases where the freezing range is long, the cavities may take the form of intercrystalline fissures.[4]

Alloys which freeze over a temperature range are prone to hot tearing at the stage in freezing when the network of primary crystals has become coherent. The contraction of the primary dendrites over the freezing range will produce ruptures in the network if the bulk contraction of the network is restrained by the mould. The danger of such hot tearing, under any given casting conditions, depends on the

constitution of the alloy.[5, 6] Thus, if the bulk of the metal is deposited as a dendritic network in the upper part of the freezing range, the alloy will rapidly reach the dangerous condition where the dendritic network is only weakly coherent, and the structure will be subjected to large strains in cooling to the solidus temperature. In such an alloy, the danger of hot tearing is greatest, and the danger increases with the length of the freezing range. If the primary network does not attain coherence until the solidus temperature is nearly reached, the contraction strains to which it is subject will be smaller and the danger of hot tearing correspondingly less. Thus, two main factors are conducive to freedom from tearing, firstly a constitution such that most of the metal solidifies in the lower part of the freezing range, and secondly a fine-grained macrostructure such that the primary dendrites do not cohere at all until solidification is well advanced.

If the metal contains dissolved gases, then these, being less soluble in the solid than in the liquid metal, will concentrate in the residual liquid during freezing until their concentration exceeds the value at which bubbles of gas are rejected from solution. In a pure metal where the liquid/solid interface is nearly plane, the gas has ample opportunity to escape through the liquid by diffusion and convection, and even if bubbles of the gas are formed, these may escape from a casting freezing from the bottom upwards. If the metal has a freezing range, on the other hand, the gas concentrates in the liquid occupying the inter-dendritic spaces, and when released has relatively little opportunity to escape from the casting. If the amount of gas is small, so that none is rejected from solution until only a small amount of liquid metal remains, the resultant gas porosity will be identical in form with that resulting from unfed freezing shrinkage. With larger gas contents, gas bubbles are formed at a relatively early stage, and these tend to attain their natural shape, i.e. spheres.[7]

IV.—Preparation of the Molten Metal.

1. *Dissolved Gases and their Sources.*

Mention was made in the previous Section of the evolution of soluble gases as one cause of the formation of internal cavities. Gas evolution during solidification is of two types:

(*a*) The rejection from solution of an elementary gas when the metal solidifies; this is due to the much higher solubility of the gas in the molten metal than in the solid.

(*b*) The formation of a compound gas on solidification by the

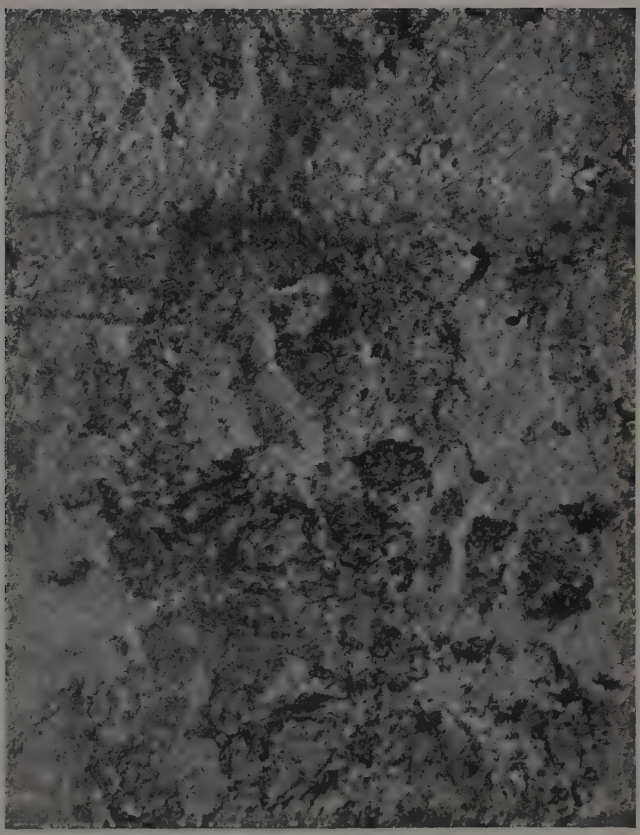


FIG. 1.—Folds Due to Oxide Films in Surface of a Brass Ingot. × 2.

[*To face p.* 292.

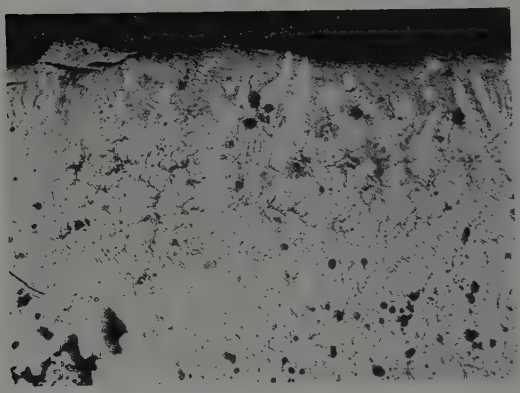


FIG. 2.—Tin Sweat on a Chill-Cast Tin Bronze. × 75.

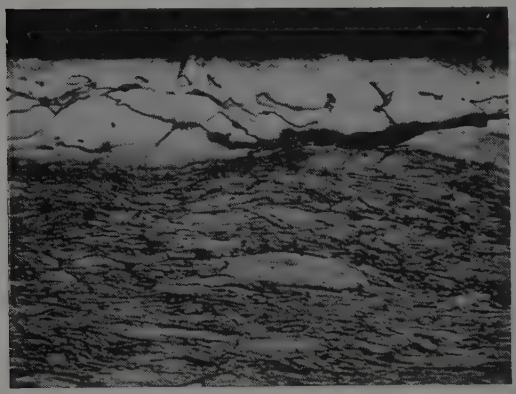


FIG. 3.—Section Through Fragmented Tin Sweat on Cold-Rolled Bronze Strip. × 300.

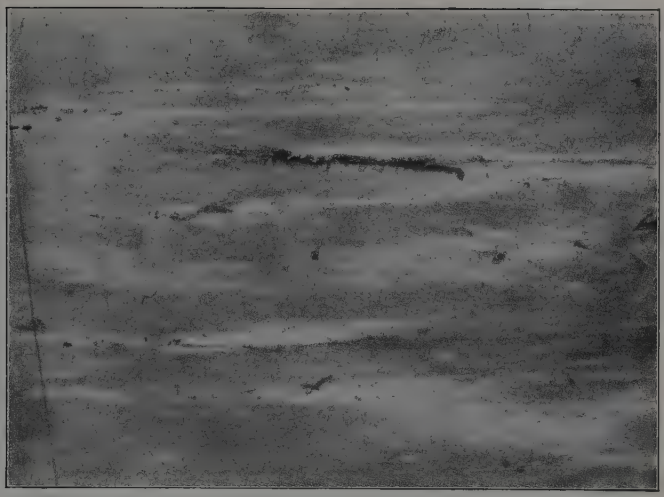
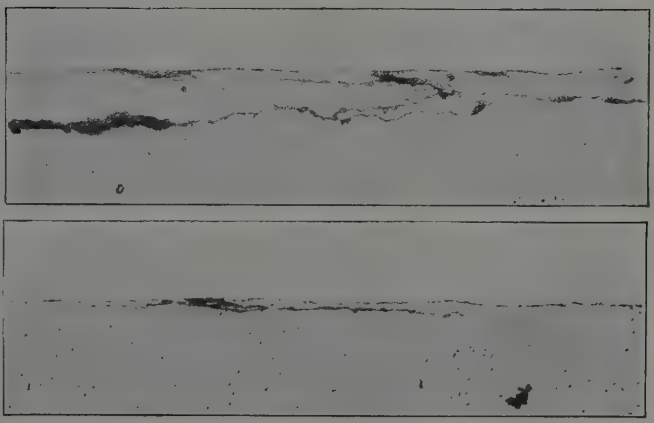


FIG. 4.—Typical "Spill" Defects in Rolled Brass Strip. × 1.



× 50.

× 100.

FIG. 5.—Micro-Sections of Typical "Spill" Defects in Rolled Brass Strip.

FIG. 6.—Crazed Surface of a Cast Iron Mould.

FIG. 7.—Refinement of Macrostructure of Brass Ingot by Volatile Mould Coating. Lower half of mould coated with soot and upper half with resin. $\times \frac{1}{3}$.

reaction of two constituents both soluble in the molten metal and at least one of them less soluble in the solid metal.

In the first of these cases the soluble gas is almost invariably hydrogen. Hydrogen is absorbed in some degree by most metals in the molten state if they are brought into contact with hydrogen, the solubility of the gas being proportional to the square root of the pressure of hydrogen in the atmosphere in contact with the melt.[8]

With most metals the solubility of the gas in the melt increases rapidly with rise of temperature until a temperature is reached at which the vapour pressure of the metal becomes appreciable. Thereafter, with increasing vapour pressure of the metal itself, hydrogen solubility

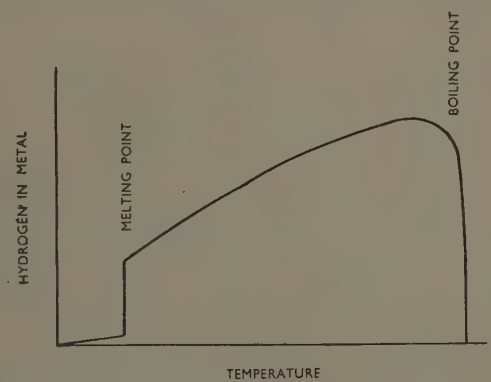


Fig. 9.—Solubility of Hydrogen in a Metal when Hydrogen Pressure Plus Vapour Pressure of the Metal Equals 1 Atmosphere.

decreases to zero at the boiling point of the metal. Fig. 9 illustrates this point and shows that the vapour pressure of the metal increases rapidly over a relatively short temperature range, with a resulting rapid decrease in the hydrogen content of the melt.

The solubility of hydrogen in the solid metal at the melting point is usually only a small fraction of that in the molten metal at the same temperature, and it is this marked change in solubility of the gas which is mainly responsible for hydrogen-gas unsoundness in the cast metal.

It does not follow that hydrogen rejected from the freezing liquid will necessarily produce porosity. The rate of diffusion of hydrogen through liquid metals is high, and in a casting freezing uni-directionally there is a strong tendency for the gas rejected from the freezing metal to diffuse away through the adjacent liquid, ultimately escaping to some

extent from the exposed upper surface of the liquid. Unlike most other elements in metallic alloys, hydrogen shows a marked tendency to segregate " normally " instead of " inversely ".

The second type of gas evolution, namely the reaction between soluble constituents forming a compound gas, is often a more important source of unsoundness. The most familiar example is that of hydrogen and oxygen in copper,[9] which recombine to form steam during solidification of the metal and thus produce " steam unsoundness " in the cast product. At a given temperature, the concentrations of hydrogen and oxygen in the liquid metal are related to one another and to the partial pressure of steam in the surrounding atmosphere, in accordance with the mass-action law, the reaction involved being :

$$2H + O \rightleftarrows H_2O$$

and the concentrations of the reactants being given by :

$$[H] \text{ in metal} = K\sqrt{\frac{p\overline{H_2O} \text{ in atmosphere}}{[O] \text{ in metal}}}.$$

It follows that an increase in the oxygen content of the bath causes rejection of some of the hydrogen as steam, the principle involved in the familiar process of degassing by oxidation treatment. The value of the equilibrium constant K decreases with decreasing temperature, and, moreover, since both oxygen and hydrogen, and especially the latter, are more soluble in the liquid than in the solid copper, the concentrations of the two reactants in the liquid phase rapidly increase and thus exceed that of the equilibrium product as freezing proceeds. Steam is then evolved and " reaction gas " unsoundness results. It has been shown [10] that sulphur and oxygen can co-exist in molten copper, and can cause unsoundness, due to evolution of sulphur dioxide on solidification, in a similar way; and the production of unsoundness in nickel-bearing alloys by the reaction between carbon and oxygen has also been demonstrated.[11]

The free hydrogen content of furnace atmospheres is usually low, and other hydrogen-bearing gases are chiefly responsible for the gas absorption by the melt in practice.

The main source of hydrogen is from the dissociation of water vapour at the metal surface, forming an oxide and liberating atomic hydrogen, which dissolves readily in the melt. The occurrence of this reaction leads to a relatively high concentration of hydrogen on the metal surface and a correspondingly high rate of solution of hydrogen, which far exceeds that which would be expected from a consideration of the free hydrogen content of the furnace atmosphere itself. Experi-

ment shows that if a melt is agitated in atmospheres containing various proportions of moisture, the gas content of the metal increases more rapidly the higher the moisture content, but the amount ultimately dissolved is the same whatever the water-vapour content and equals that dissolved, very much more slowly, from a 100% dry-hydrogen atmosphere. This result implies that when the internal gas pressure exceeds one atmosphere, bubbles are formed and escape, even though the concentration of atomic hydrogen at the reacting surface is equivalent to that produced by several atmospheres of molecular hydrogen.

It is not to be assumed that the furnace atmosphere is the sole source of contamination by hydrogen or other gas-forming elements. Clearly, they can be, and often are, present in the constituents of the furnace charge. Carbon, sulphur, and oxygen commonly enter the melt *via* the components of the charge, and even hydrogen sometimes enters in this way, either as dissolved hydrogen, e.g. in cathode copper, or as hydrated corrosion products on the surface of ingot material, e.g. in aluminium-base and magnesium-base alloys.

One of the commonest sources of hydrogen is moisture (combined or free) present in the linings of ladles, and since the amount of water required to cause severe gassing in this way is extremely small, drastic firing of the ladle surface, or, better, washing with molten metal, is essential to avoid gas pick-up at this stage in the casting process.

2. *Removal of Dissolved Gases.*

As the importance of gas contamination was realized, attempts were made to avoid gas pick-up, e.g. by avoiding as far as possible a reducing atmosphere in the furnace, and by fast melting and other means whereby the opportunities for contamination of the melt were minimized. While such measures are desirable, gas contamination cannot be altogether avoided thereby, and to ensure optimum and controllable results, some method of removing the gas from the melt is necessary. The use of these methods, however, should not lead to carelessness in melting, as, obviously, the more gas pick-up is avoided at that stage, the better.

The most important step in the preparation of the melt for pouring is therefore to ensure sufficient freedom from dissolved gas or from elements capable of reacting to form gas unsoundness. The principles to be followed in securing this freedom from gas contamination will be fairly obvious from what has been said above.

Firstly, if the gas in solution is in equilibrium with an atmosphere containing a certain amount of the soluble gas, then, obviously, removal

of all soluble gas from the atmosphere in contact with the melt will lead to the evolution by the metal of its gas content. If this evolved gas is continually swept away, more gas will diffuse into the atmosphere until equilibrium is reached at the zero gas content of both metal and atmosphere.

In the second type, where the constituents cause reaction, one of these constituents is always oxygen in the known cases of reaction unsoundness. If oxygen could be completely and effectively removed from the melt, sulphur and carbon would not in themselves lead to any gas evolution, although they may have other undesirable effects; and the harmfulness or otherwise of the residual hydrogen content would depend on the amount present.

The removal of hydrogen from the melt by diffusion into an inert furnace atmosphere is not quite so simple as it sounds, because not only must the atmosphere be free from hydrogen and hydrogen-containing gases (e.g. water vapour), but the metal surface must be sufficiently clean and free from oxide films, &c., to enable the gas to diffuse into the atmosphere. Moreover, the larger the surface of metal exposed to the atmosphere the more rapidly will the hydrogen be removed. In the case of copper, phosphor bronze, &c., there is little difficulty, because the surface of these metals carries only a little fluid slag, which does not prove a serious barrier to gas diffusion. All that is needed, therefore, is provision of a clean dry atmosphere, of, for example, nitrogen or carbon dioxide, which is preferably bubbled through the melt to produce a large interfacial area.[12]

Metals which form a strong oxide skin which can constitute a barrier to gaseous diffusion, such, for example, as aluminium, need a rather more drastic treatment. Aluminium can in fact be degassed by scavenging with an inert gas such as nitrogen, but the process is a little slow and difficult to carry to completion. This is due to the difficulty of getting cleanliness of surface through which diffusion can occur, a situation that can be remedied to some degree by covering the surface with a flux capable of dissolving or absorbing the oxide film, since it seems the flux itself does not constitute such a serious barrier as does the oxide skin.[13] Best of all and most generally used, however, is the purging of the melt by bubbling through it an active insoluble gas capable of reacting with the oxide of the metal and converting it to a volatile or fluid substance. Chlorine treatment of light alloys is a case in point. In this case, the possibility exists that the hydrogen is removed as hydrogen chloride, but in fact the published data for the free energies of the chlorides of aluminium and hydrogen at the temperatures involved make it practically certain that combination between

hydrogen and chlorine is negligible and the degassing is effected by the scavenging mechanism.

Reaction-gas unsoundness can usually be most satisfactorily dealt with in two steps. The first step is an increase in the oxygen content by deliberate oxidation to a sufficiently high degree to remove hydrogen, sulphur, and/or carbon.[11, 12, 14] It is possible, theoretically, to eliminate the reactants by lowering the partial pressure of the reaction gas in the surrounding atmosphere to nil, but in practice this would require agitation to produce an adequate degree of degassing in a reasonable time. When oxidation treatment is used without such agitation, the concentrations of the reactants probably attain values in equilibrium with one atmosphere of the reaction gas, in other words, the reaction gas is evolved as bubbles, and when this evolution ceases, further change in the melt is relatively slow. Consequently, degassing is more rapid and more complete the higher the oxygen concentration in the melt.[12] The second step is to remove excess oxygen, which can be done readily by the use of powerful deoxidizers such as phosphorus or, in the case of nickel-bearing alloys, magnesium or even calcium. The melt should then be in a condition where it is relatively free from oxidizable elements and substantially free from oxygen.

A small amount of residual deoxidant is desirable because, as indicated in an earlier paragraph, any oxygen and reducing element remaining in the melt tend to concentrate in the residual liquid during freezing until their contents exceed the equilibrium product. In the presence of residual deoxidant, the oxygen content of the liquid cannot increase in this way,[15] because any such increase leads to precipitation of the oxide of the deoxidizing element. Thus, the presence of the residual deoxidant provides a margin of safety, allowing the reducing element of the compound gas to concentrate to a greater extent in the residual liquid before the equilibrium product is exceeded. The choice of deoxidant is restricted by two considerations, firstly, that it shall have a higher affinity for oxygen than the other constituents of the melt, and secondly, that the deoxidation product shall be liquid and therefore able to aggregate and separate readily from the melt.[16] Of the deoxidizers commonly used for non-ferrous metals, phosphorus deserves special mention because the deoxidation product, a fluid phosphate slag, so admirably fulfils the second of these requirements.

3. *Removal of Non-Metallic Inclusions.*

There are obviously other undesirable constituents besides gaseous ones which need to be eliminated before the melt is in a sufficiently clean condition to produce good castings. Mechanically entangled oxides,

slag, fluxes, &c., which find their way into the ingot and get entrapped therein are an obvious source of weakness. Metallic oxides are the most obvious source of contamination as they are often present in the raw materials charged, and in any case are likely to form to some degree on the charge before it melts down. If the oxide is completely insoluble in the molten metal, it does not follow that the oxide particles readily float and can be eliminated. Differences in specific gravity are generally considerable, but extremely minute particles cannot be separated easily from the melt, which is in a state of considerable thermal agitation.

Insoluble oxides can be removed by agitating the melt in contact with a flux which dissolves, or at least wets, the oxides and which has physical properties permitting it to separate readily from the melt. If the oxide particles react with added deoxidants to form fluid products, the deoxidants may be expected to remove both dissolved oxygen and undissolved oxides; this probably occurs to some extent when phosphorus is added to a bronze melt contaminated with stannic oxide inclusions.

The mechanism involved in the action of fluxes which remove non-metallic particles from metal melts has received little attention. It has been shown in some cases that effective fluxes are not necessarily capable of dissolving or decomposing the non-metallic inclusions to any considerable extent, and thus it is probable that many fluxes, particularly those employed in removing refractory oxides like alumina, &c., perform their function by the physical process of wetting the non-metallic particles and causing them to enter relatively large masses of the flux, which, if suitably constituted, readily separate from the metal bath.

While considering the removal of impurities, the possibility of introducing new impurities from the equipment used must not be overlooked. For example, the use of unprotected iron stirrers and skimmers will lead to unnecessary iron pick-up in many alloys.

V.—Casting Methods.

Having applied the principles described above to produce a bath of molten metal free from gases and other undesirable constituents, the next step is to transfer this metal without re-contamination into a mould giving the required shape.

1. *Open-Slab Casting.*

The simplest type of casting for subsequent working is the open slab, and this is still used extensively in the non-ferrous metal industry.

From the discussion of the freezing process in an earlier Section it

follows that pure metals and alloys with short freezing ranges will develop localized shrinkage, i.e. a pipe, if they are cast into relatively narrow, open-topped moulds. For such materials, the use of open moulds is restricted to wide slabs where solidification is mainly from the bottom upwards, with relatively little side-wall effect. Tough-pitch copper is a notable exception, where the steam evolution during freezing counters the tendency to pipe; in this case relatively narrow open-topped moulds can be used.

In alloys which freeze over a wide temperature interval, slabs cast in open moulds are porous in the upper layers because feeding liquid drains from these layers to feed the freezing shrinkage in the layers nearer the chilled bottom. The porous zone is deeper the longer the freezing range of the alloy, so that the open-slab casting method is restricted to alloys of fairly short freezing range. Rapid solidification minimizes the depth of the porous zone, and since the rate of solidification of the upper layers decreases rapidly with increasing thickness of the slab casting, the depth of the porous zone is relatively small in thin slabs. Attempts to encourage rapid solidification from the bottom are referred to on p. 306. The two main advantages of the open-slab method are: firstly, the low cost of the mould and the fact that pouring is rapid, a big advantage in some production units, and secondly, that the metal stream is short, so that injection of air, &c., into the metal is negligible and consequently the casting is free from gas porosity from this source.

2. *Top Pouring.*

The vast majority of billets and ingots in non-ferrous metals for working are produced by pouring the metal into a mould from the top. An enormous variety of sizes and shapes are produced, varying from relatively squat ingots to wire-bar castings 7 ft. long $\times$ only 4 or 5 in.^{2} cross-sectional area.

(a) *Surface Effects.*

The method of pouring from the top introduces some difficulties as regards surface quality, but offers some advantages in respect of freedom from internal defects due to shrinkage. The alternative method, frequently used in steel-making, of pouring from the bottom through a fireclay runner on which the mould stands, is hardly ever used other than experimentally in the non-ferrous industry, partly because it is expensive when applied to relatively small ingots, and partly because it tends to flatten temperature gradients in the casting when pouring is completed, and thus decrease the directionality of solidification.

From the point of view of surface quality, the most important con-

sideration is the introduction of the metal into the mould as tranquilly and as gently as possible, and bottom running achieves this successfully. Top pouring, on the other hand, inevitably causes a certain amount of splashing and turbulence in the molten pool. These harmful effects have to be minimized as much as possible.

The first essential is to pour at a high temperature, so that there is no tendency to premature solidification while the metal is in a disturbed condition. Rapid pouring achieves the same result in another way, in that it allows less time for the metal to cool before it has become tranquil in the mould. Thus, the general requirements for avoiding folds and for remelting any splashes are high temperature and a rapid pour.

Everything that is said here, however, about the rate of pour, &c., must be related to the size and shape of the ingot in question. The smaller the cross-section of the particular casting, the more important will it be to pour fast and hot to secure a good surface, because of the greater chilling rate of the small volume of metal.

The second essential is to direct the pouring stream so that it does not fall down one face of the mould. Impingement of the stream on the mould surface produces non-symmetrical turbulence in the metal, which impairs surface quality; the equally harmful consequence of overheating the mould face is referred to later. For good surface quality, therefore, the mould should be quite vertical, and the pouring stream should be directed vertically and accurately down the axis of the mould cavity.

Finally, to obtain a good surface it is important in any metal forming a solid oxide skin to avoid oxidation of the stream during pouring and of the rising surface of molten metal within the mould. Any skin of oxide which forms around the stream of metal or on the surface of the liquid in the mould will inevitably be stirred into the metal or folded against the mould wall by the rising liquid surface. The more turbulent the pouring, the more serious these effects, and alternative remedies are possible. The first is to add a deoxidant to the metal which produces surface-oxidation products of a less harmful type (for example, fluid phosphate films on phosphorus-deoxidized bronze), which ultimately appear in part in the casting as relatively innocuous spherical inclusions. The second is to coat the surfaces of the mould with a volatile reducing agent such as oil of some type, which fills the mould cavity with gases in which the metal stream will not oxidize.

The success of these methods depends entirely on the readiness with which solid oxides are formed on the molten surface. In the case of aluminium, which oxidizes even in the presence of carbon monoxide, attempts to protect the metal from oxidation by an inert atmosphere are doomed to failure, and for metals and alloys containing such

elements with a high affinity for oxygen, alternative casting methods which involve tranquil pouring must be adopted, as described in later paragraphs.

(b) *Internal Soundness.*

Freedom from shrinkage effects can only be secured by ensuring that solidification proceeds from the bottom upwards, and it is impossible with some of the castings made industrially to ensure internal soundness in top-poured ingots. Unless special methods are adopted to effect directional cooling, such as are referred to later, directional solidification can only be secured by pouring so slowly that one layer virtually solidifies while the next relatively thin layer is being poured in.[1, 4, 14] Thus, slow pouring gives conditions approaching the ideal ones described in earlier paragraphs.

Internal soundness requires not only good feeding and the absence of dissolved gases, but also the avoidance of entrapped gases during pouring. The entrapping of gases in top pouring is particularly liable to occur with ingots of narrow cross-section, which solidify rapidly. If the mould is standing vertically, the stream falling into the pool of liquid metal penetrates according to its momentum and carries with it bubbles of gas from the mould atmosphere. These gas bubbles are swept down at the periphery of the pouring stream and consequently move outwards and later rise nearer the walls of the casting where solidification is more advanced. Thus, the bubbles are particularly likely to be entrapped just under the skin of the casting. The old practice of pouring brass ingots in moulds which were sloping at 20° to 30° to the vertical was particularly bad from this point of view, because the bubbles of gas carried into the ingot inevitably rose under the inclined-lid side of the mould, where they were readily entrapped by the freezing metal.[1]

The less the momentum of the falling stream, the less will be the penetration, and the shorter distances, therefore, will the bubbles have to rise to effect their escape. It is advantageous, therefore, to pour a given volume of metal in a number of small streams rather than in one large one. The use of a pouring bowl or tundish with a number of holes distributed along the centre line of the cross-section of the casting is the easiest way to effect the necessary distribution of the metal in a number of small streams. The length of the holes in relation to their diameter is important and should be large enough to ensure adequate direction of the metal stream. For the same reason, the depth of metal in the tundish should be as great as possible, so that the metal entering the holes has no considerable lateral velocity.

Thus, the use of a number of small pouring streams instead of one

large one is not only conducive to freedom from trapped gases, but also approaches the ideal freezing condition, in which thin layers of metal are added tranquilly in smooth succession.

In practice, the combination of a relatively high pouring temperature and a low pouring speed is found to give the best compromise between the conflicting requirements of freedom from shrinkage defects and freedom from surface defects and "trapped gas" porosity. The effects of pouring temperature and speed on the soundness of brass ingots are summarized in Fig. 10, which clearly shows the importance

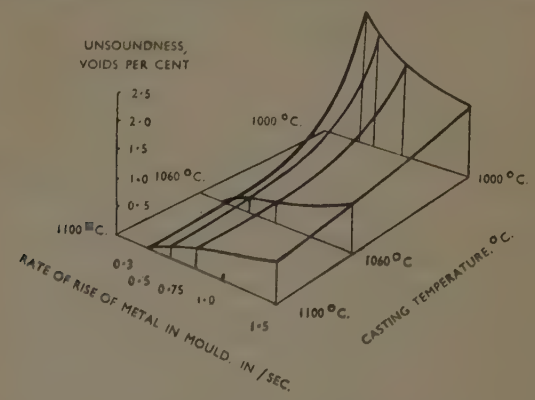


FIG. 10.—Effect of Rate of Pouring and Casting Temperature on Soundness of Top-Poured Brass Ingots.

of pouring hot enough to avoid air entrapment, and slowly enough to avoid shrinkage cavities.

The chilling effect of the tundish puts a lower limit on the diameter of the individual pouring stream, and the loss of heat from the crucible or ladle imposes a lower limit on the total through-put of the group of streams.

While what has been said above is generally true, it must be quite clear that different metals, even for instance different copper alloys, need entirely different methods of treatment. For example, phosphor bronze can be poured much more slowly than brass without detriment to surface quality; and the alloy with a small freezing range, e.g. 60 : 40 brass, can be more readily made free from shrinkage unsoundness than can tin bronze or 70 : 30 brass, and may therefore be poured faster to secure improved surface quality.

An important, and in some cases overruling, consideration is the desirability of casting large ingots, even though the final product may be required in short lengths. Large ingots are obviously necessary in some cases, because long lengths of wire or large sheets are required in one piece. Even, however, where short lengths are ultimately required, modern rolling plant makes it economical to break down a large ingot rapidly, subsequently cutting short lengths as required. This is, on the whole, a substantial advantage from the point of view of the casting, in that a large but short and thick ingot offers a much better proposition from the casting viewpoint than the long thin ingots that were at one time so commonly the starting point in the manufacture of wrought copper alloys.

(c) *Mould Materials.*

For many years cast iron was almost exclusively the mould material used for the production of ingots and billets for subsequent working. Cast iron is easy to produce in the required shape and with a smooth surface. The quality of cast iron varies enormously, but there is no clearly defined specification for cast iron for ingot moulds other than the general, probably true belief that a hæmatite iron is desirable on the grounds of low phosphorus content.

It has long been known, however, that cast iron is subject to one major failing, namely a tendency either to crack completely through the section, or more commonly to form small cracks all over the inner surfaces. The major crack splitting the mould is generally the result of either bad design involving unduly sharp corners, or of residual internal stresses in the casting which are added to the stress induced when the metal is poured. Such internal stresses should be eliminated by initial annealing of the cast mould, followed by slow cooling.

Shallow cracking of the inner faces of cast iron is inherent in the properties of the material and the treatment it receives. When molten metal at, say, 1100° C. is poured into a cast iron mould, the inner faces of the mould heat rapidly to 500°–700° C., depending on the circumstances.[17] The tendency of the inner faces to expand must be prevented by design and by clamping in order to maintain the shape of the cavity. The high stresses in these inner faces are therefore relieved by plastic flow at high temperature, and on subsequent cooling tensile stress is developed in the inner faces. On account of the low ductility of cast iron at ordinary temperatures, these stresses produce minute transverse cracks on the inner face, and repetition of the cycle gradually causes these cracks to expand. Fig. 6 (Plate XXX) shows this crazing in an advanced stage.

Some qualities of iron are undoubtedly rather more resistant to this type of crazing than others, but all grey irons will fail in this way in due course.

If mild steel is used instead of cast iron, the tensile stresses on the inner face tend to cause warping rather than cracking; and in any case mild steel has other disadvantages, such as a tendency to stick to copper-base alloys.

Cast iron also possesses another disadvantage, in that when the mould is grossly overheated, as, for example, by impingement of the stream, the oxide skin unavoidably present on the mould face reacts with the carbon in the iron, giving off carbon monoxide, which forms blow-holes in the ingot surface.[17] The solution to these problems is the use of copper for the majority of industrial non-ferrous metals and alloys. The high conductivity of a copper mould ensures greater uniformity in temperature throughout the mould wall, and if a relatively thin copper mould face is used with water cooling, the working surface itself always remains relatively cool. This is the ideal method for using copper as a mould material, because it gives a long life of mould, freedom from cracking with its consequent detrimental effects on ingot surface, freedom from gas evolution from the mould face, and a large output from any one particular mould, which can be used again and again at short intervals. Although the heat diffusivity * of copper is more than twice that of cast iron, the use of a copper mould instead of cast iron does not greatly reduce [17] the solidification time. Other factors, including the effect of mould dressings and air-gap formation, are obviously important.

(d) *Mould Coatings.*

Whatever mould is used, however, some coating on the inner face is necessary, firstly to prevent adhesion of the casting to the mould, and secondly to reduce the initial surface chill on the thin film of metal which first washes over the mould face. If the extreme surface layers solidify too rapidly, they will be rippled to an unacceptable degree. Various coatings are used, therefore, the functions of which are as follows :

(i) To reduce initial surface chill on the molten metal.

(ii) To protect the mould face and prevent adhesion of the molten metal to the mould.

(iii) To provide, when desirable, an atmosphere of reducing gas within the mould and around the stream of metal.

The first two of these functions can well be provided by an inert

* Heat diffusivity $= \sqrt{\text{conductivity} \times \text{density} \times \text{specific heat}}$.

mould coating such as bone ash, which is used with great success in the casting of high-conductivity copper, and lamp-black, which is effective with many materials. It is clearly important that the mould coating should " stay put " and should not wash off in flakes or lumps which become embedded in the ingot. For this reason, the inert coating must be thin and is preferably bonded with some resinous or clay binder. Where the reducing atmosphere is also needed and the dressing is a convenient way of applying it, a large variety of oils are used. Seal oil, rape oil, resin, &c., all find favour, but there seems no good scientific basis for preferring one to the other.

3. *Non-Turbulent Pouring.*

All the remarks above are primarily intended to apply to top-pouring of ingots and billets direct from the furnace or crucible. It has been indicated that such methods of pouring produce turbulence, and that with some alloys, particularly those containing aluminium, turbulence is likely to have disastrous effects on the ingot surface. Special methods have, therefore, been developed for pouring such ingots, some of which have proved transient, but some of which have been used extensively.

The simplest of these methods, and one which was until recently widely used for the production of aluminium alloy rolling slabs, was the pouring of the molten stream down an edge of the mould, initially inclined at an angle of about 70° or more to the vertical. As the mould fills, it is gradually rotated into a vertical position so that the incoming metal flows in a gentle stream down the mould edge without splashing, but with, of course, a considerable amount of internal turbulence.

This has been improved upon from the point of view of ingot quality, but with some detriment to ease of production, in the Durville process, in which the metal is transferred to a ladle mounted with the mould on a rotating table. The edge of the mould cavity and the inner surface of the ladle are in the same plane, so that when the assembly is rotated about a suitable axis, the metal flows tranquilly into the mould. Much has been written of the Durville process from the experimental point of view, but apart from Durville's original paper,[18] no description of the industrial use of this method has been published.

Zublin's method of tranquil pouring [19] deserves mention, although it does not appear to have been applied in practice on a large scale. In this method, one edge of a vertical ingot mould is open and the metal is poured through this opening into the mould cavity *via* a suitable launder. The mould is slowly lowered during pouring, and its open edge is progressively sealed by a series of plates linked together in a continuous looped chain.

4. *Practical Approaches to Directional Solidification.*

A variety of methods has been tried in which extreme measures are taken to promote directional solidification.

Perhaps the most extreme resort is the process described as " immersion casting ",[20] in which a water-cooled plate is lowered into a bath of molten metal and a slab is formed by crystallization on to the cooled plate.

One of the simplest and earliest attempts to secure directional freezing was what is known as the " tin can " method,[21] in which the metal is poured into moulds consisting of thin steel cans, the heat capacity of which is too small to effect solidification. When the " mould " is full of molten metal in a tranquil condition, it is lowered slowly into water, or through water sprays, and a considerable measure of longitudinal solidification results. This, of course, is only applicable to relatively low-melting-point materials, but it has been used extensively for aluminium alloys, where the fine structure obtained by the rapid cooling has facilitated subsequent working, particularly forging.

The Erical horizontal water-cooled mould is an interesting case of an attempt to utilize the advantages of horizontal casting by increasing the solidification speed with water-cooling of the base plate and making the sides of the mould from metal of relatively low conductivity.[22] Examination of a 72 : 28 brass (50° C. freezing range) slab cast in this way showed that the lower two-thirds of the ingot were virtually sound, while the upper one-third contained a good deal of finely dispersed porosity, totalling about 2·5% voids. Unless all this was machined off, it gave rise to large numbers of fine spills in rolled strip, which would not be acceptable in high-quality material.

The more important development of directional solidification is in the continuous and semi-continuous casting methods used to a limited extent for copper alloys and almost universally for aluminium and aluminium alloys.

For copper alloys, the Junghans–Rossi method [23] is the one mainly used, although there have been other continuous-casting methods developed and employed with some success in the U.S.A. In the Junghans–Rossi machine, which is widely used for the casting of 60 : 40 brass extrusion billets, the mould is a chromium-plated copper cylinder, about 18 in. long for a 7-in.-dia. billet, externally water cooled. The metal is poured continuously through a special device in the top of the mould, and the latter first moves downwards at the same speed as the billet and then is moved upwards rapidly after a travel of about 2 in. Oil is sprayed into the top of the mould from time to time to minimize

adhesion between the billet and the mould. Much of the heat is removed by this method through the walls of the copper mould, and to this degree solidification is lateral rather than longitudinal; but the hot billet issuing from the bottom of the mould is liberally sprayed with water, and in this way longitudinal solidification is promoted to ensure good feeding. The solid–liquid interface is nevertheless cup-shaped, but the solidus and liquidus surfaces are so close together that feeding is extremely good, and ingots of great soundness and homogeneity are produced.

The semi-continuous or direct casting [24] of aluminium alloys is effected in a similar way, but with much shorter moulds, commonly made of aluminium or one of its alloys. The shorter mould used in this method ensures still more cooling from the bottom relative to the sides, and solidification is more strongly directional along the longitudinal axis.

Other methods of continuous casting, such as the Asarco method of the American Smelting and Refining Company,[25] and the Wellblund Benard machine used by the United States Metals Refining Company,[23] have certain special advantages. For instance, the Asarco method allows the casting of much smaller sections than is customary by other continuous methods, with a high dimensional accuracy, and both methods are used successfully for the casting of copper.

All these methods of pouring, particularly the direct casting of aluminium alloys, involve such rapid cooling after solidification that large internal stresses are developed in the casting, and casting speed is largely determined by this factor. The occurrence of these stresses is due, of course, to non-uni-directional heat extraction, and the temperature isothermals observed or calculated [26] in such castings show that solidification is in fact far from uni-directional.

Nevertheless, there can be no doubt that these processes approach more nearly to the ideal requirements of a casting process than any of the older methods, and they are steadily supplanting the older methods for the casting of non-ferrous ingots for subsequent working. The vertical fall of the metal into the mould is short, so that the problem of mechanically entrapped gases and oxides does not arise. At the same time, sufficient heat is extracted from the metal in the desired axial direction to prevent "bridging", and the resulting casting is notable for its internal soundness. Apart from the internal stresses mentioned above, which in some alloys may cause cracking during cooling below the solidus temperature, the main fault with such castings is their relatively poor surface quality, but even here the defect is a surface and not a sub-surface one, and the casting may be machined and made virtually free from such defects.

VI.—Structure.

1. *Macrostructure.*

The macrostructure of cast metals has, in some cases, an important influence on their behaviour in subsequent working, and in others is of no material consequence. The factors controlling the macrostructure are still imperfectly understood, but for pure metals, in which the composition of the first-deposited solid is not appreciably different from that of the remaining liquid, the macrostructure of a chill-cast ingot frequently consists of a narrow chilled layer comprising numerous small crystals with random orientation, and adjacent to this layer a columnar zone which frequently persists to the centre of the ingot. It is known that the columnar zone has a marked preferred orientation,[27, 28] which arises from the fact that the rate of crystal growth is more rapid in certain crystallographic directions than in others. The chilled-layer crystals originate from a large number of nuclei formed in the under-cooled metal adjoining the mould face, and certain of these crystals, whose preferred direction of growth is parallel to the direction of heat abstraction (i.e. normal to the mould wall), are able to grow preferentially, and do so at the expense of their neighbours. The feature of the columnar zone apparent on inspection, i.e. the great length of the crystals in relation to their cross-section, arises from the fact that the lateral growth of the crystals is quickly arrested when they touch one another.

In pure isotropic metals, this preferred orientation is of little importance from the point of view of the subsequent behaviour of the ingot in working, but in metals with more complex lattice structures, for which the number of planes of easy slip is limited, the preferred orientation is usually undesirable. In the familiar case of zinc slabs for rolling, for example, this preferred orientation causes difficulty in cold working,[29] and it is usual to raise the working temperature to a point where more numerous slip planes are available for deformation.

In alloys which freeze over a temperature range, the macrostructure tends to be finer, and the columnar zone is largely or completely replaced by equi-axial grains. In this case, the solid which first separates from the melt differs in composition from the remaining liquid, and therefore in the vicinity of the first-formed crystals there is a layer of liquid whose composition differs from that of the original liquid. The liquid in this layer is of lower melting point than the original liquid; thus, in effect, the growth of the first-formed crystals is restricted by the concentration gradient around them, and the liquid of initial composition outside the concentration gradient is able to under-cool to a point where new nuclei

are formed; consequently, the final structure tends to be an equi-axial one.

The extent to which this concentration gradient refines the grain-size depends, of course, upon the constitution of the alloy, i.e. upon the slopes of the solidus and liquidus lines, which determine the magnitude of the initial gradient; upon the rate of solidification, which governs the time available for diffusion to dissipate the gradient; and lastly upon the specific properties of the alloying elements (for example atomic radius), which govern the ease with which they can diffuse through the liquid and so dissipate the gradient.

The effects of these factors are superimposed upon one another, and it is not surprising that no empirical rules have yet been devised which will predict the type of structure to be expected in cast alloys. The position is further complicated by the fact that there is reason to believe that foreign nuclei, i.e. particles of compounds dispersed through the melt, exist in commercial metals and alloys and are capable of acting as centres of crystallization. The existence of such nuclei is indicated by the observed effects of superheating liquid metals; in this connection it is usually the case that superheating tends to coarsen the macro-structure of the cast material (magnesium–aluminium alloys provide a notable exception). Other fortuitous effects also influence ingot structure; it has been suggested, for example,[1] that the pouring stream in top-poured ingots may detach small solid crystals from dendrites which have already formed in the mould and may disperse these through the remaining liquid and provide potential centres of crystallization which influence the macrostructure. Clearly, turbulence during pouring and the start of solidification has an important effect: even the gas evolution from a volatile mould coating may profoundly affect the structure of a 70 : 30 brass ingot of thin section [1] (Fig. 7, Plate XXX).

In some non-ferrous metals, it is known that small additions of certain elements have a powerful grain-refining effect, but the precise mechanism involved has not yet been established, and the question is still the subject of study. On the whole, our present knowledge of means for controlling the macrostructure of cast metals and alloys leaves much to be desired.

2. *Microstructure.*

Microstructure of cast metals is usually less sensitive to the conditions of solidification than the macrostructure. In general, a fine and uniform microstructure in ingots for subsequent working is required, partly because such structures are conducive to good working behaviour, and partly because the final properties of the worked product are considerably affected by the distribution of the second phases, &c. Refer-

ence has already been made to the importance of grain-boundary area when the alloy contains impurities or other constituents of relatively low melting point at the grain boundaries. A decrease in grain-size will, of course, tend to reduce the concentration of the harmful constituents at each grain boundary, and thereby minimize any damaging effects on the working behaviour of the material.

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THE PRODUCTION OF REFINED-COPPER SHAPES.* 1157

By R. H. WADDINGTON.†

SYNOPSIS.

This paper describes the procedure employed at a modern works for the production of standard and special shapes of electrolytic tough-pitch high-conductivity copper. Operations preceding melting and casting of refined shapes are briefly outlined. A more detailed discussion covers early reverberatory-melting practice, and the later adoption of direct-arc-type electric furnaces for melting purposes.

Variations in cathode structure influence the characteristics of the cast shape. Optimum deposition conditions are secured by control of the electrolyte and the use of addition agents.

Melting processes in the electric furnaces are conducted so that diffusion of gaseous products from the metal bath may readily occur. A controlled quantity of air is drawn through the furnace chamber to facilitate this process and impart to the molten metal an oxygen content of about 0·01%. Pouring methods for both horizontally cast and vertically cast shapes are considered, with an account of the use of intermediate ladles, funnels, and mould dressings. Copper moulds are used for all shapes; those for horizontal shapes are solid castings of the tray type, while internally-water-cooled moulds are employed for vertical casting. Control methods during melting are reviewed, as well as the inspection procedure maintained to ensure highest quality of product.

Machining operations comprise cropping of vertically cast cakes, billets, and wire bars, milling of a tapered nose on the latter shape, and drilling of a centring cup in billets used for piercing.

I.—INTRODUCTION.

THE International Nickel Company of Canada, Limited, in its Copper-Refining Division Works at Copper Cliff, has carried on since 1930 the extensive processing involved in refining blister copper into the standard and special shapes of electrolytic tough-pitch high-conductivity copper. This division of the Company's operations was formerly known as the subsidiary, Ontario Refining Company, Limited, from which name is derived the " ORC " brand and trade-mark identifying the Company's copper products.

This paper has as its scope a description and discussion of the melting of copper cathodes and subsequent casting into refined-copper shapes at Copper Cliff. Although previous papers [1, 2, 3] have described the various operations at this works, a very brief outline of the principal

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sequences is given below, preparatory to dealing with the subject proper.

Molten blister copper is poured from converters at the Copper Cliff smelter into hot-metal transfer cars, which are hauled 1½ miles by electric locomotives, to the anode furnace department of the refinery. Within the building the cars are moved by an endless-cable mechanism, to three 300-ton reverberatory furnaces. The molten charge in each car, weighing about 50 tons, is poured into the furnace which at that time is accumulating metal, and when a full charge has been reached a refining treatment is commenced. When gaseous and certain other impurities have been reduced to the desired level the furnace is tapped and the charge cast into 580-lb. anodes for the electrolytic department.

The electrolytic department is housed in a spacious structure, 480 × 340 ft., containing 1350 depositing cells, each capable of producing 700 lb. of cathode copper per day. Under the influence of electrical energy the anodes are dissolved in the copper sulphate electrolyte and pure copper is deposited on the cathode. Precious metals and base-metal impurities fall to the tank bottom as a sludge, which is collected and treated for the recovery of the values contained. The pure copper cathodes are systematically withdrawn, washed, and transported to the melting and casting department for conversion to the cast copper shapes of commerce. A minor percentage of copper is marketed directly in cathode form.

II.—The Requirements of Refined-Copper Shapes.

Tough-pitch copper shapes of acceptable quality must be free from non-metallic inclusions, fissures, or blow-holes. Any porosity must be very fine, uniformly distributed, and confined to the region immediately beneath the set surface. The latter should be of minimum area, substantially level or slightly crowned. Other surfaces must be free from laps, cold sets, inclusions, or other miscellaneous imperfections which would cause defects in the fabricated product. Dimensional variations should be of low magnitude, and chemical purity and composition well above specified minimum standards. The attainment of optimum standards in respect to these characteristics requires extremely close control at every stage of the production process.

In the first few years of the operation at Copper Cliff, melting and casting practice was similar to that used by other copper refiners. Fuel-fired reverberatory furnaces were charged to capacity with copper cathodes and revert material; a melt-down period then ensued, following which the molten charge was refined, in order to remove impurities

introduced from the fuel, furnace atmosphere, skimming tools, and other sources. Once the charge had been brought to the correct "tough pitch", it was cast as speedily as possible in order that the desirable properties so attained might be reflected in the cast shapes before deterioration of the optimum "pitch" condition. In the production of horizontally cast wire bars, ingots, and ingot bars, very high casting rates are attainable, and a charge of more than 300 tons may be taken out in 4–5 hr. Even in this short time, however, and in spite of protective coke or charcoal coverings, the copper bath tends to increase in impurities, notably from the furnace atmosphere. Again, many vertically cast shapes must be poured at substantially lower rates than the horizontal variety, and under more exacting conditions, and this tends to increase the difficulties inherent in reverberatory-furnace melting.

As a steadily increasing proportion of the copper shapes produced at Copper Cliff were of the vertically cast category, investigations were launched to determine if electric-arc furnaces could be adapted for copper melting. The successful outcome of this work led, during the period 1936–38, to extensive plant changes, providing for the production of all shapes from refined copper melted in such furnaces, two of which have been installed.

III.—Electric-Arc Furnaces for Melting.

The characteristics of the arc furnace, adapted to copper melting, permit a simplified operation by comparison with previous reverberatory-furnace practice. No refining sequence is required, no slagging process is involved, and standardized optimum conditions are readily reproduced and maintained. Heat is carried to the bath by radiation from the arc flame, by reflection from the roof and side-walls of the melting chamber and, to a lesser degree, as the result of resistance to the current through the molten copper between the electrodes. The temperature of the bath is kept within close limits by maintaining regular rates of metal charging and power input.

The electric-furnace melting section contains as its principal items of equipment: two three-phase 25-cycle direct-arc "Lectromelt" furnaces 15-ft. in dia., each capable of melting more than 15 short tons of copper per hour; two enclosed pour hearths heated by means of low-frequency induction; and two 40-ft. dia. casting wheels equipped to take the 36 different types of moulds normally required.

The refractory lining of the arc furnaces has been designed with a

view to durability and freedom from contaminating constituents. At and below the metal line a fused monolith of high magnesia content contains the 30-ton bath. Roof and upper side-walls are constructed of chemically bonded magnesite brick.

The 18-in.-dia. furnace electrodes which conduct the 4000 kVA. required at capacity operation are made of high-purity graphite. Total ash-forming constituents of the electrodes amount to less than 0·50%, and the iron content is below 0·10%. Electrode consumption varies with the melting rate, and for the operation described averages slightly under 4 lb. per short ton of copper melted.

The control board for the melting operation contains the usual switchgear, relays, meters, and, in addition, the recording and controlling pyrometric equipment. A view of the control board for No. 2 furnace is shown in Fig. 1 (Plate XXXI). A more detailed description of the installation as a whole is given in a previous paper.[4]

The metal outlet of each furnace is connected to a well-insulated and protected launder system. Copper flows down these launders to the cylinder-shaped pour hearths, which hold about 5 tons of metal and provide for smoothing out variations in flow rate and temperature before discharging the copper to mechanically actuated tilting ladles.

Control of pour-hearth flow, ladle operation, and wheel movement is centralized in the pourer's operating stand. The mechanical units involved are designed to give smoothly accelerating or decelerating motion, which in the case of the wheel drive is obtained with a fluid transmission.

The melting process is continuous. Prime-quality copper cathodes weighing 265 lb. are charged at a typical rate of two per minute through a slot-shaped opening at the rear of the furnace. The charge slot is so designed that the cathodes enter the melting chamber with sufficient momentum to submerge them beneath the bath, which is kept at a fairly constant volume of 30 tons. Under normal circumstances no covering is used on the bath. Under the displacing action of the cathodes, metal flows continuously from the furnace tap-hole down the launder into the pour hearth. In this vessel there is a theoretical retention period of 15–20 min. under conditions which permit temperature stabilization, and pitch control if necessary. From the pour hearth, copper flows into single- or multi-lipped tilting ladles, and thence either directly or through refractory funnels to the moulds. Before describing the casting procedure, it is appropriate to review the technical control imposed up to this stage.

IV.—Technical Control of Charge Material and Melting Process.

At Copper Cliff, control commences with the basic charge material. Shortly after the commencement of electric-furnace melting a study was instituted, having as its object the correlation of variations in cathode structure with variations in the characteristics of the final cast product. This study has proceeded continuously and includes a comprehensive photomicrographic record of cathode structure, which has shown quite clearly that for the desired results in respect to refined shapes, cathodes must be dense, unusually smooth, have a fine compact crystal structure, and be as free as possible from striations.

Nodulation of cathodes gives rise to inclusions of electrolyte and float slimes particles, difficult to remove; a coarse crystal structure results in intercrystalline deposits of organic and other substances, as well as occluded sulphate solution. Comparative freedom from these undesirable characteristics is possible by the use of clear, relatively gas-free electrolyte, to which there is continuously added small, controlled quantities of reagents that promote the desired cathode structure. These addition agents include animal glue, calcium lignosulphonate, oil emulsant, and sodium chloride. As a result of these additions and other measures taken in the electrodeposition process, the amount of gaseous or gas-forming constituents in the charge material is kept to a minimum.

The next step is to perform the melting operation in such a manner that there is little or no contamination from the furnace atmosphere, but with the safeguard that there is provision for diffusion, from the metal bath, of gaseous products if present. This process is facilitated by drawing a controlled and variable quantity of air through the melting chamber, sufficient to ensure that the furnace atmosphere consists mainly of carbon dioxide and nitrogen. In addition to providing a flowing, controlled atmosphere, the air drawn through the furnace imparts to the metal bath an oxygen content which normally averages about 0·010%. It has been determined that this amount of oxygen is desirable in order to minimize the influence of the hydrogen present. It has been stated above that the furnace atmosphere is essentially nitrogen and carbon dioxide. This is brought about by combination of the oxygen in the air with graphite from the electrodes. Fractional percentages of oxygen, hydrogen, and water vapour are also present, and carbon monoxide averages less than 4%. A typical analysis of the furnace atmosphere is: CO_2 16·8, CO 3·1, O_2 0·6, H_2 0·5%, H_2O n.d., N_2 remainder.

The amount of air admitted to the furnace is varied according to the

oxygen content of the bath. Determination of this is made by optical methods, on samples taken from the furnace tap-hole every 20 min.

In accordance with requirements depending on atmospheric conditions, the type of casting being produced, and other considerations, a " trimming " control may be exercised by adjusting vents in the launder connecting furnace and pour hearth. These adjustments cause an increase in the cuprous-oxide content of the metal and promote degasification.

A sparse cover of graphite granules is used in the pour hearth, to protect the bath from further oxidation, and in the tilting ladle charcoal is used. The final adjustment to casting pitch is made by stirring this charcoal covering so that increased contact with the molten copper is obtained. Occasionally a small green brand may be inserted beneath the bath in the pour hearth for very short periods.

The measures taken to ensure production of internally sound cast shapes are based on the assumption that unsoundness results chiefly from the following reactions :

$$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$$

and

$$H_2 + Cu_2O \longrightarrow 2Cu + H_2O$$

In respect to the unsoundness caused by the first of these reactions, the precautions taken to minimize electrolyte impurities in or on the cathodes, together with the non-contaminating nature of the melting process, result in a reduction of defects due to this cause to an insignificant frequency.

The unsoundness arising from the reaction of hydrogen with cuprous oxide is also capable of control. Allen [5] has demonstrated that this reaction is most vigorous just when the copper–copper-oxide eutectic is solidifying; it follows therefore that if, in addition to the steps already taken to minimize hydrogen content, the rate of solidification is high, then the opportunity for the formation of blow-holes from this cause is diminished. The use of water-cooled copper moulds is effective in bringing about a high solidification rate.

The possibility of unsoundness resulting from the solubility of carbon in molten copper was the subject of a study published some years ago by Bever and Floe [6] who found that the solubility of carbon in molten " oxygen-free " copper just above its melting point is about 0·0001%. The authors pointed out, however, that this proportion of carbon is, at that temperature, equivalent to a volume of CO or CO_2 equal to almost 10% of the volume of copper, and that oxidation of this carbon during casting may cause porosity.

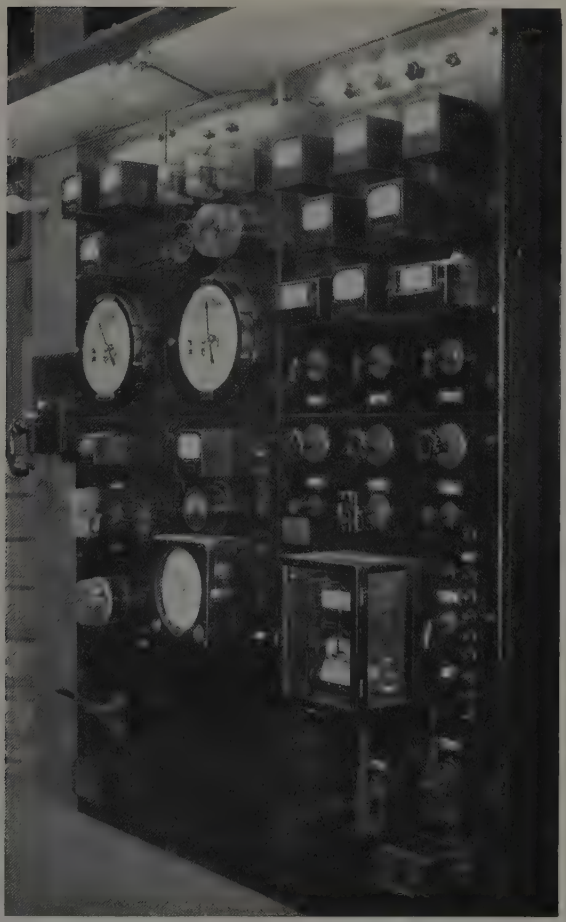

FIG. 1.—Control Board for No. 2 Electric Furnace.

[*To face p.* 316.

Fig. 2.—Intermediate Pouring Equipment.

Left: Double-outlet hand ladle. *Right:* Conical funnel with nozzle outlet.

FIG. 3.—Pouring Arrangement for Horizontally Cast Wire Bars.

FIG. 4.—Pouring Arrangement for Circular Billets.

The Copper Cliff process presumes that the solubility of carbon in copper containing about 0·01% oxygen is probably too low to be of practical significance.

V.—Pouring Operations.

Primary considerations in the mechanics of transferring copper into the moulds are that the metal stream be accurately directed so as to avoid impingement on the mould wall, the rate of flow be under close control, and the falling stream be possessed of cohesive tendencies. These precautions, with others to be described later, minimize the occurrence of such surface defects as mould-wash inclusions, laps, and cold sets.

In the production of certain shapes, copper is poured directly from the tilting ladle into the mould. Many other shapes, however, require the interposition of refractory funnels or small hand ladles with nozzled outlets. In the pouring of vertically cast wire bars, for example, a double-outlet hand-ladle is used to serve each pocket of a double mould. The pourer, by means of long handles, inclines the hand-ladle so that, at the start of the pour, metal accumulates therein. After a few seconds the level position is resumed, and full-bore, properly centred, streams of metal then flow through the outlet nozzles, which have a square orifice. Circular billets are poured with the aid of a conical refractory funnel having an integral nozzle outlet similar in shape to that used for the square wire bars. Both types are shown in Fig. 2 (Plate XXXII).

Cakes, also vertically cast, are poured from the tilting ladle without the use of intermediate refractory contrivances, although other means are used to guard against surface defects. As each metal stream from the tilting ladle breaks over the ladle lip, it is caught in a small long-handled metal bowl shaped like the pouch of a pelican, from which the device receives its name of "pelican ladle". Continuously engaging the metal stream, the operator quickly lowers the ladle to the bottom of the mould cavity, where it is emptied and provides a liquid pool into which the stream from the tilting ladle now falls with little or no splash. This procedure is known as "floating" and has proved effective in combating surface defects.

The so-called regular shapes, horizontally cast wire bars, ingot bars, and ingots, are poured directly from tilting ladles into shallow tray-type moulds. A refinement in pouring wire bars of this type is the use of electrically heated ladle lips, which permit casting at the low temperature dictated by technical considerations for this shape. Without

external heat the copper tends to form skulls in the lips, and this alters the profile and consequent shape of the stream and results in a variety of surface defects. The pouring arrangements for horizontally cast wire bars and circular billets are shown in Figs. 3 and 4 (Plates XXXIII and XXXIV) respectively.

VI.—Mould Dressing.

The mould wash used for all types of electrolytic tough-pitch copper shapes is an aqueous suspension of well calcined, finely ground bone ash. This material is not wetted by copper, contains little or no volatile constituents, and imparts no impurities to the metal. The density of the suspension must be varied for different types of shapes. Thus, in the case of horizontally cast wire bars a suspension having a density of about 6·5° Baumé is used, and for vertically cast cakes a typical figure is 30° Baumé. The method of application also varies; a long-handled spray gun proves most suitable for the wire bars, but in the production of cakes the wash is simply flowed evenly over the mould-cavity surface downwards from the top perimeter. It is desirable in the case of large cake moulds to superimpose a second layer of mould wash around the top 4–6 in. of the mould. This is sprayed on and prevents the occurrence of exudations, or "sweating", from the casting. The copper slabs forming the mould bottoms receive a coating of bone-ash emulsion applied with a brush.

Careful attention is given to the water used for making up the mould wash, to make sure that it is free from organic matter and low in suspended or dissolved mineral substances. Needless to say, grease- or oil-contamination also makes such water unsuitable for the purposes under discussion. The manner in which the mould wash attaches itself to the mould surface, and thereby performs its function, is also dependent on the mould temperature. As is well known, metal surfaces heated above a certain temperature will repel water, owing to the formation of spheroidal drops held away from the hot face by a layer of steam. If a mould is allowed to reach this condition, it is not possible properly to apply the bone-ash dressing. On the other hand, if the mould is too cold the wash will be streaky, and incomplete volatilization of the water when the mould is next filled will cause porosity or possibly an explosion. The mould temperature varies for different shapes, but in general is sufficiently high to volatilize all water in a few seconds.

The production of phosphorus-deoxidized copper shapes calls for an entirely different mould wash, and much lower mould temperatures are generally employed. In place of water, a heavy mineral oil is used as the vehicle for either bone ash or bone black. The solid constituent,

together with the necessary volume of oil, is placed in a pebble mill, and a smooth, uniform suspension is formed after several hours' mixing. Stored in specially heated containers to maintain constant viscosity, the mixture is applied to circular billet moulds by means of a felt-disc swab. Cake moulds receive the application by means of rectangular swabs covered with lambskin. Mould temperature prior to pouring is maintained at approximately 95° F. (35° C.).

VII.—Moulds for Vertical Casting.

Reference has been made above to vertically cast shapes. As the name implies, this type of shape is cast in moulds having the mould cavity in a vertical plane and so designed that the oxidized set surface of the cast shape forms one of the surfaces of minimum area. In the subsequent rolling operation, cakes which have been cast in this manner are generally rolled end-wise, so that the oxidized set is confined to one end of the strip or sheet. The mould cavity is accurately machined with a highly finished surface, opposite faces being either parallel or substantially so. This condition also aids the mill processing by ensuring uniformity of section and smooth surface.

The special-shapes moulds used at Copper Cliff are manufactured in the refinery's own shops. Cake and billet moulds are made from electrolytic tough-pitch H.C. copper to which silver has been added to maintain surface quality during the life of the mould. They are drilled to provide a system of connected internal channels for the circulation of cooling water.

Moulds for the production of machine-pointed vertically cast wire bars are made by encasing specially produced square copper tubes in steel jackets. Suitable baffles are provided within the steel casing, and an expansion joint gives relief in respect to the difference in movement between copper tube and steel jacket. As with the channelled moulds, provision is made for the circulation of cooling water, in this case between the cooling jacket and the copper tube.

When assembled on a casting wheel each mould is connected to an upper and lower header, which encircle the wheel and which in turn are connected to service mains by means of a rotary swivel joint at the wheel centre. Water enters at the bottom of the mould and is drawn off at the top. The ring of moulds so assembled forms part of a closed circuit which also includes a heat exchanger, surge tank, and centrifugal pumps. The heat exchanger consists of a number of large copper blocks, each drilled with a multiplicity of internal passages and connected in parallel. Cooling water and mould-circulating water flow

through alternate passages but in entirely separate circuits. Thus the heat which has been transferred from the cast shape to the mould is taken away by the mould-circulating water, which in turn is finally relieved of its thermal load by the external cooling water flowing through the heat exchanger. The quantity of heat energy removed by this system varies according to pouring rate and type of shape, but is approximately 500,000 B.Th.U./ton.

VIII.—Standard Production Methods.

As the result of investigations into the relationship between internal soundness and the conditions required to achieve this, it has been possible to determine a standard operating procedure for the production of each class of copper shape. The copper is brought to the pouring point in an optimum state from the point of view of gaseous and other impurities, and important considerations which now come into play are metal temperature, mould temperature, and pouring speed. The overall objective is to obtain a rate of solidification which is not so rapid as to cause shrinkage cracks or voids, but on the other hand has sufficient speed to be essentially uni-directional and to deter reaction-unsoundness.

Methods of maintaining metal-temperature control involve the use of optical, radiation, and thermocouple pyrometers. The temperature of metal just after leaving the arc-furnace tap-hole is continuously recorded by means of a circular-chart-type pyrometer connected to a Chromel–Alumel couple protected by a Carbofrax tube. A somewhat similar instrument records the metal temperature in the low-frequency induction-heated pour hearth, although in this case a sensitive lens-type Rayotube unit actuates the pyrometer, which provides automatic control. Frequent checks on these instruments are made by disappearing-filament-type optical pyrometers sighted on the metal stream leaving the pour hearth or tilting ladle.

Mould-temperature control is, in the case of the internally cooled type of mould, effected by automatic control of the circulating-water temperature. A thermostatically operated valve controlling the cooling-water flow to the heat exchanger is set for the temperature desired, and maintains this condition. Actually it is not practical to keep constant the temperature of the mould itself, which during the pouring and solidifying periods shows an increase of 15° to 30° F. This has no harmful effect and, considerably in advance of being refilled, the mould and mould-circulating-water temperatures are again equal. A typical temperature curve for the casting sequence of a 4 × 16 × 35 in. cake is shown in Fig. 5. In this example, copper at 2050° F. (1121° C.) is

poured slowly during the floating operation, and then at an accelerated rate until the mould is within 4 in. of being filled, from which point the rate is reduced until pouring is finished; the total elapsed time is 2 min. The temperature of the mould-circulating water rises from an initial value of 205° F. (96° C.) and reaches its maximum of 235° F. (113° C.) 3 min. after pouring starts. Solidification of the copper is complete

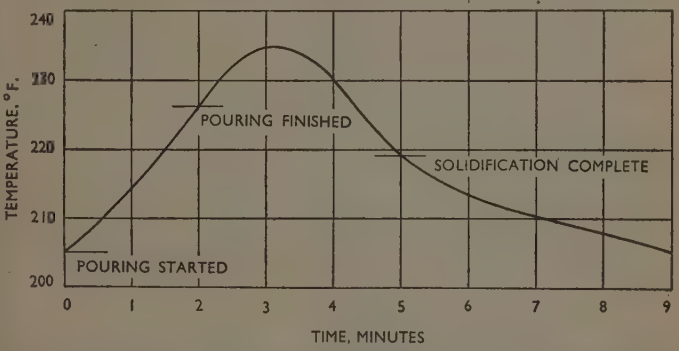

Fig. 5.—Typical Mould-Cooling Water–Temperature Curve for Casting Sequence of 4 × 16 × 35 in. Vertically Cast Cake.

at the end of 5 min., and the shape is discharged to a boshing tank some 19 min. later. Shortly thereafter the mould-water temperature has returned to 205° F.

IX.—Records and Inspection.

A continuous record is kept of pertinent chemical and physical data collected during the melting and casting operations, and against these data are matched the observations made from an extensive examination of sample shapes. In the case of cakes, small sectional slices are cut, to permit macro-examination for soundness, several times during an 8-hr. shift. The larger sizes undergo a further check, in which a whole cake is machined to half its original volume in a plane parallel to the major surface, this test being made once a day. Density determinations are made on the complete shape in the case of wire bars and billets, and on part sections for other sizes. Sample deoxidized billets are subjected to a breaking test by means of a hydraulic press, to show up any internal shrinkage cracks. Variations from the norm revealed by these and other controls are checked with the conditions obtaining at the time of production, so that the standardized production procedure may be modified to meet changed conditions. Portions of weekly summary

Table I.

WEEKLY METALLURGICAL DATA SHEET.

No. 2 Electric Furnace. Week ending 16 May 1948.

Date.	Production No. and Shift.	Shape.	Temperature, ° F.					Oxygen Content (Optical).					Pour Rate, lb./min.	Analysis of Castings.		Good Work, %.	Principal Rejects.
			Launder.		Pour Hearth.	Ladle Average.	Moulds Average.	Tap-Hole.		Pour Hearth.				Cu, %.	O_2, %.		
			Max.	Minimum.				Max.	Average.	Max.	Average.	Minimum.	Average.				
May 14	906 A	1000 lb. V.C. cake	2195	2095	2080	2045	194	0·020	0·010	0·017	0·017	0·015	356	99·961	0·030	97·3	Bone ash.
	B	" " "	2200	2100	2080	2049	197	0·015	0·010	0·017	0·015	0·015	345	99·961	0·031	99·6	
	C	" " "	2200	2100	2080	2049	200	0·015	0·010	0·017	0·015	0·015	345	99·960	0·032	97·9	Bone ash—cold sets.
May 15	907 A	" " "	2210	2100	2080	2049	192	0·013	0·010	0·020	0·015	0·013	347	99·959	0·033	95·1	Bone ash—cold sets.
	B	" " "	2200	2110	2085	2050	197	0·013	0·010	0·015	0·015	0·013	341	99·958	0·033	97·8	Charcoal inclusions.
	C	" " "	2200	2100	2085	2049	200	0·013	0·010	0·017	0·017	0·013	345	99·959	0·033	99·6	
May 16	908 A	" " "	2210	2110	2085	2053	196	0·017	0·013	0·020	0·017	0·015	341	99·959	0·032	100·0	
	B	" " "	2200	2100	2080	2049	200	0·015	0·010	0·017	0·015	0·015	345	99·961	0·032	97·0	Conveyor bruises.
	C	" " "	2195	2095	2080	2045	196	0·013	0·010	0·017	0·015	0·015	345	99·957	0·033	99·6	

WEEKLY PHYSICAL DATA SHEET.

No. 2 Electric Furnace. Week ending 16 May 1948.

Date.	Production No. and Shift.	Shape.	Density.	Macroscopic Examination of Structure.				
				Sample Cross-Section.			Broken Section (Billets).	Full Machined Section.
				No. 1.	No. 2.	No. 3.		
May 14	906 A	1000 lb. V.C. cake	...	Porosity—nil	Porosity—nil	Porosity—nil	...	Sample A2. Set—slightly crowned.
	B	" " "	...	" "	" "	" "	...	Negligible sub-set porosity.
	C	" " "	8·71	" "	" "	" "	...	
May 15	907 A	" " "	...	" "	" "	" "	...	Sample A1. Set—slightly crowned.
	B	" " "	...	" "	" "	" "	...	No visible porosity.
	C	" " "	8·69	" "	" "	"	...	
May 16	908 A	" " "	...	" "	" "	"	...	Sample A1. Set—slightly crowned.
	B	" " "	...	" "	" "	" "	...	No visible porosity.
	C	" " "	8·70	" "	" "	" "	...	

Waddington :

reports recording operating conditions and results of tests are shown in Table I.

During the actual production operation a systematic inspection is carried out for the detection of casting defects other than those concerning internal structure. After being discharged from the mould the shape is cooled in a bosh tank, from which it is carried by a system of conveyors through the inspection line, where it is examined by trained personnel. Although inspection procedure varies in detail according to the type of shape being cast, a rigid check is exercised on every shape, to ensure adherence to the refinery standards for surface characteristics and dimensional tolerance. Most works' specifications at Copper Cliff are more exacting than those of the British Standards Institution or the American Society for Testing Materials; in no case are they less strict.

The inspectors remove from the conveyor and segregate those shapes which fall below standard. The reason for rejection is indicated by chalk mark and tallied in record form on a large tally board which can be readily seen by the casting foreman. Superficial blemishes are removed by chipping or grinding and, if on re-examination no further defect is revealed shapes so treated are passed on as accepted. The inspection crews work under shift foremen who report to the Chief Inspector, but the latter official may not modify any established standards without authorization from the Refinery Superintendent. Every shape is stamped with symbols denoting date, shift, and shift period during which it was cast. This permits ready co-ordination of recorded technical and inspection information against production results at any particular period of time. Summary studies are made of these data from time to time and operating procedures either maintained or modified according to interpretation.

X.—Machining Operations.

A minor proportion of cakes is diverted by the inspector to be cropped at either top or bottom. Tops are cut for low set, bruises, or dimensional variation. Bottoms are cut for cold sets, indentations incurred in dropping on to the conveyor, and for exceeding length specifications. Cakes so cut are re-inspected and if blow-holes are detected the shape is rejected. Phosphorus-deoxidized and silver-bearing cakes are all cut at both top and bottom ends as a general procedure, and subjected to similar re-inspection.

Billets, both electrolytic and phosphorus-deoxidized, are cut to specified lengths on a special sawing machine which removes both top and bottom sections simultaneously. When specified for piercing,

billets are cupped by drilling a shallow bore in one end, which is used to centre the mandrel of the piercing machine. Billets produced for extrusion processes are not cupped, but are cut to short lengths as required by the purchaser. All billets are scrutinized after cutting, for indications of unsoundness, before receiving final approval.

Vertically cast wire bars range from $3\frac{1}{2} \times 3\frac{1}{2}$ in. to $6\frac{1}{2} \times 8\frac{1}{2}$ in. in cross-section. The majority are subjected to a special machining operation which cuts a streamlined tapered nose or point on each end, to facilitate entry into the various passes of the breakdown mill. An intensive investigation of design and forming methods, conducted prior to the introduction of these pointed wire bars, resulted in the development of a highly specialized automatic milling machine. Tests since observed by refinery officials, and results reported by wire-mill operators, indicate that a significant improvement has been achieved in comparison with the former blunt-end wire bars. Specifically, this is reflected in sharply lowered percentages of end scrap and elimination of underfilling.

XI.—General.

At the present time some 55 types and sizes of special shapes are being produced at Copper Cliff, and new items are being developed regularly in accordance with the requirements of customers. For instance, in addition to cakes, wire bars, and billets of electrolytic tough-pitch copper, these shapes are also produced in the form of phosphorus-deoxidized copper with residual phosphorus contents ranging from 0·007 to 0·060%.

For the consumer who desires to increase the temperature at which recrystallization takes place in his fabricated article, without impairing other important physical properties, silver-bearing copper is produced. Pure electrolytic silver is added in controlled amounts to the metal bath, to give silver contents ranging from 10 to 30 troy oz./ton.

In addition to a well equipped works laboratory employing some 25 technicians, the resources of the Company's Central Research Laboratory are regularly utilized in process control and development work.

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1. R. H. Waddington, *Canad. Chem.*, 1940, **24**, 164.
2. *Canad. Min. J.*, 1946, **67**, 446.
3. *Canad. Min. Met. Bull.*, 1948, **41**, (434), 362.
4. R. H. Waddington and J. C. Bischoff, *Trans. Canad. Inst. Min. Met.*, 1946, **49**, 199.
5. N. P. Allen, *J. Inst. Metals*, 1930, **43**, 81.
6. M. B. Bever and C. F. Floe, *Trans. Amer. Inst. Min. Met. Eng.*, 1946, **166**, 128.

MELTING AND CASTING ALUMINIUM BRONZE INGOTS FOR SUBSEQUENT WORKING.* 1158

By A. J. MURPHY,† M.Sc., F.I.M., Vice-President, and
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Synopsis.

Decisive factors in techniques for casting ingots of aluminium bronze for subsequent working are the short freezing range and the tenacious film of oxide which forms on the molten metal. This film protects the metal from absorption of reducing gases during melting: the indiscriminate use of fluoride fluxes is therefore undesirable. The oxide film gives rise to surface defects on ingots cast with turbulent pouring but it enables a surface of exceptionally good quality to be obtained when non-turbulent methods of casting, such as the Durville process, are employed. The Durville method is limited to ingots having a length : diameter ratio of not more than 8 : 1. Accurate control of composition is necessary in forgeable aluminium bronzes and is assisted by hardness testing.

I.—Composition.

By aluminium bronze is meant a copper-base alloy in which, after copper, the principal alloying metal is aluminium. The members of the series intended for use in the wrought form may be divided into those suitable for cold working, as by cold rolling and drawing, and those suitable for hot working, as by hot rolling, extruding, and forging. In the cold-working bronzes the aluminium content is not more than 9%, i.e. somewhat below the upper limit of the alpha solid solution at the ordinary temperature; the aluminium bronzes capable of hot working have aluminium contents ranging from about 9% to about 14%. Bronzes with higher proportions of aluminium than this find no industrial application.

Most of the aluminium bronzes contain other elements besides copper and aluminium: the principal are iron, nickel, manganese, zinc, and silicon. The proportion of any one of these is rarely more than 5%.

II.—Physical Characteristics.

The physical characteristics of the aluminium bronzes relevant to a consideration of melting and casting are the density, temperatures of liquidus and solidus, latent heat of fusion, thermal conductivity, and volume change on solidification.

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The relatively low density resulting from the presence of the aluminium is quite important in the bronzes containing about 10% aluminium, the density of which is 10% lower than that of the industrial brasses and tin bronzes; this has to be borne in mind in practice when esti-

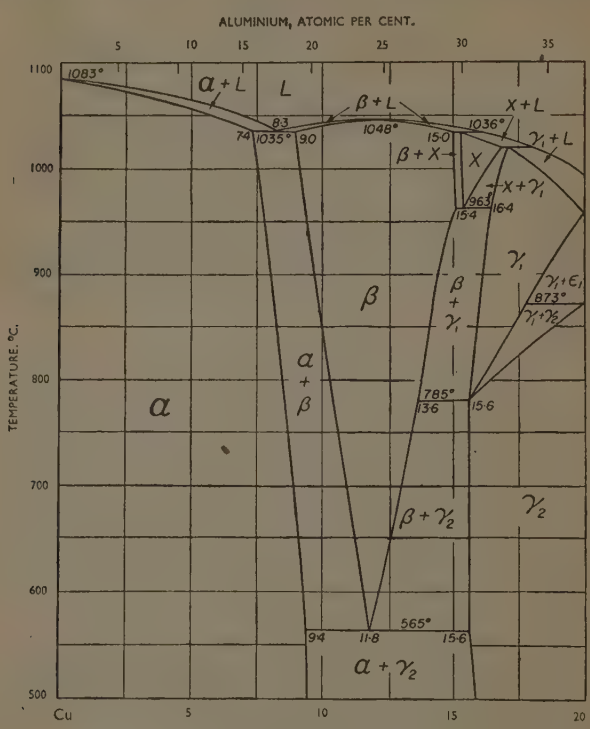

FIG. 1.—Copper–Aluminium Equilibrium Diagram; 0–20% Aluminium. (From *Metals Handbook* (*Amer. Soc. Metals*).)

mating the weight of aluminium bronze to be produced from crucibles and billet moulds, the capacities of which are often rated in terms of brass.

Fig. 1 shows the relations at the liquidus and solidus in the binary aluminium bronzes, i.e. the simple copper–aluminium alloys. Over the whole range of composition comprising the aluminium bronzes the

alloys are characterized by a short freezing range. This is zero at the eutectic composition 8·3% aluminium, solidifying at 1035° C., and in the beta phase at 12% aluminium, where there is a maximum on the liquidus curve at 1048° C. Liquidus and solidus are not separated by more than 10° C. in the binary aluminium bronzes. In the important quaternary bronze to specification D.T.D. 197A containing aluminium 10, nickel 5, iron 5%, copper remainder, the liquidus temperature is 1080° C. and the solidus 1065° C., a range of 15° C.

When these characteristics are compared with those of the brasses, it is seen that while the temperatures of fusion are higher in the aluminium bronzes (e.g. copper 90, aluminium 10%, 1040° C.; copper 60, zinc 40%, 900° C.), the melting ranges are not dissimilar—up to 10° C. in the aluminium bronzes and up to 20° C. in the brasses. In both cases the range is much smaller than in the tin bronzes (e.g. tin 7%, 160° C.), aluminium alloys (e.g. copper 4, magnesium 0·5, manganese 0·5%, 100° C.) and magnesium alloys (e.g. aluminium 8·5, manganese 0·3%, 100° C.). The narrow freezing range has the effect of accentuating the tendency for a deep central pipe to form in a vertically cast cylindrical ingot unless special measures are taken to maintain the feeding head liquid to a late stage.

Reliable data on the latent heat of fusion appear to be lacking for aluminium bronzes, as for other copper-base alloys. The thermal conductivity of the aluminium bronzes at 20° C. is distinctly lower than that of the brasses; for the 90 : 10 copper–aluminium alloy the value is 0·144 cal./cm.²/cm./°C./sec., and for a complex nickel–iron–aluminium bronze 0·09, while for both 70 : 30 and 60 : 40 brass it is 0·29. The volume change on solidification is of the order of 5%, not greatly different from that of the industrial brasses.

III.—Oxide Films.

The aluminium bronzes provide a striking example of a family of alloys characterized by attractive mechanical properties and yet dependent for effective industrial exploitation on the development of special techniques in casting. As long ago as 1907 Carpenter and Edwards in the Eighth Report to the Alloys Research Committee of the Institution of Mechanical Engineers showed that on account of their strength, hot-working properties, and corrosion-resistance, the aluminium bronzes were of great potential importance to engineers. Attempts to cast ingots of aluminium bronze by the methods and with the equipment commonly employed in the brass industry, however, gave irregular and disappointing results. The difficulty arose from the tenacious film of

oxide which formed on the surface of the molten bronze. Once this skin was broken on pouring the metal into an ingot mould it became entangled in the casting, producing a rough, wrinkled surface and inclusions of oxide in the interior of the ingot. Fig. 3 (Plate XXXV) illustrates the appearance of such an inclusion in a photomicrograph of nickel–iron–aluminium bronze at a magnification of 500 diameters.

The methods of casting aluminium bronze in moulds of all materials are dictated almost entirely by the characteristics of the oxide film. The film forms rapidly in air both at normal and elevated temperatures. Its presence on the molten metal is normally not discernible until the surface is disturbed; if the oxide layer is caused to fold over it takes on the appearance of a thin skin of dross. The film appears to have a high " surface tension ", but this apparent film strength may be due in part to the very high rate of formation of the skin on freshly exposed molten metal.

IV.—Melting.

The two stages in the production of ingots (or billets, as they are commonly named in some districts) for subsequent working are, firstly, the melting of the metal and, secondly, the casting of the ingot. The film of oxide which provides the major problem in the casting stage is also of decisive importance in the technique of melting. If its role is properly appreciated, this thin layer of oxide can be almost entirely beneficial in melting. This is a consequence of the effective barrier it presents to the passage of furnace gases into the melt.

Hydrogen is highly soluble in molten aluminium bronze[1]: the solubility at 1100° C. is approximately one-half of that in copper, and, as in copper, there is an abrupt reduction in solubility on solidification. The circumstances are therefore favourable for the development of pin-hole porosity in the ingot if any considerable amount of hydrogen is absorbed during the melting of the metal. Practical experience shows, however, that if the oxide film is allowed to form on the molten metal and is not removed or disturbed, there is no occurrence of pin-holing, unless there is gross overheating or the metal is retained molten for a very long time. The simplest explanation of this observation is that the film is sufficiently impermeable to prevent hydrogen and other gases from gaining access to the molten metal except at a very slow rate.

If the oxide film is removed, as for instance by the use of fluxes containing alkaline fluorides, this protective action can no longer be exerted, gas passes into the metal and pin-hole porosity is observed unless the ingot is very rapidly chilled. It follows that fluxes may be worse than useless if applied to the melt from which ingots are to be cast. The use

of fluoride fluxes may be justified in remelting drossy skimmings, swarf, and residues, in order to reduce losses due to entanglement of valuable metal in the non-metallics, but it is not uncommon in such cases to see the metal " rise " in the open, shallow moulds into which it is cast. In order to de-gas such ingots it is necessary to remelt them under flux and bring them into an atmosphere free from reducing gases, where they may remain molten for a sufficient length of time to permit the escape of dissolved gas.

V.—Casting.

P. H. G. Durville in France realized at an early date that the solution of the problem of obtaining aluminium bronze ingots of good surface and free from entrapped oxide skins was to be found in a process of transferring the molten bronze from the melting vessel to the ingot mould without breaking the surface of the liquid. His British Patent No. 23,719 of 1913 gave an account of the system of casting, the " coulée tranquille ", or " still casting ", which has become known as the Durville process. Because it may justly be termed a classic in metallurgical technology, and also because it is a model of lucid exposition, the patent specification is quoted extensively in the following paragraphs.

" In casting processes where the metallic liquid is poured into the mould in the form of a stream, the height of fall, which is the difference existing between the level of the liquid in the pouring ladle and that in the mould, causes eddies and makes an intermingling of the fluid mass with included slag and other oxidizing particles, and also with air, inevitable. Pouring in a liquid stream has also the defect that the casting can only proceed slowly, from which there ensues the risk of a partial solidification of the liquid while pouring, and of an interruption in the continuity of the liquid stream, the consequences being further oxidation and inclusion of air and lack of homogeneity in the solidified ingot.

" To overcome these drawbacks it has been proposed to first pour the liquid metal into a vessel furnished with a movable stopper in its bottom. When the metal has settled the stopper is lowered and the liquid metal is drawn quietly into the mould.

" Various methods according to which the pouring vessel, containing the liquid metal, and the mould are simultaneously tilted so as to transfer the liquid metal to the mould have also been proposed, but all these differ from the present invention in that the lips of the pouring vessel and the mouth of the mould are not arranged in the same straight line, a break in the upper surface of the liquid metal and a pouring must therefore take place.

"The process according to the present invention differs fundamentally from known processes, by reason of this that the metallic liquid is first

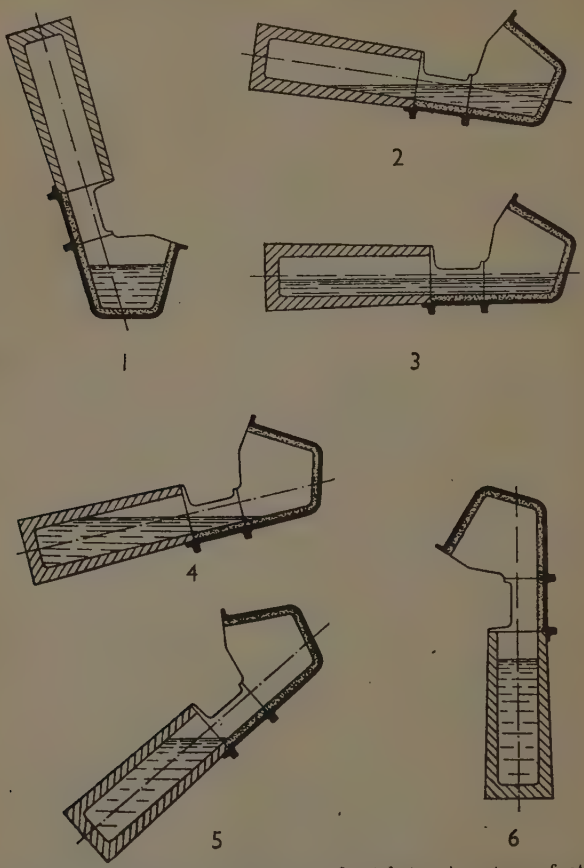

FIG. 2.—Durville Casting Process. Position of metal at various stages of rotation. (From "The Casting of Brass Ingots" by Genders and Bailey, British Non-Ferrous Metals Research Association, 1934.)

introduced into a reservoir or pocket and is then transferred from said reservoir into the mould without any change of altitude. The surface of the metallic liquid in the reservoir and in the mould remains horizontal

and continuous throughout and there is no real pouring of the liquid mass of metal but only a change in the position assumed by the metallic liquid, without any change of direction on the part of the metallic surface. By means of the new method, the casting process can go on very quickly, and nevertheless—since there is no fall, and the surface of the liquid remains in the same position throughout—no intermingling of the metallic liquid with slag or other oxidizing particles, or with air, occurs, especially since the liquid is protected therefrom by the layer of oxide remaining throughout in a horizontal position on the surface of the liquid."

The apparatus for carrying out the process consists of a combined reservoir and mould, the two being rigidly attached together in such a way that the pouring-out surface of the reservoir and the pouring-in surface of the mould lie in the same straight line, the connecting passage between the reservoir and mould being of uniform sectional area, that is, the sectional area of the mouth of the reservoir corresponds to the internal diameter of the mould.

Fig. 2 shows a typical example—in section—of the apparatus serving to carry out the process, in the different working positions.

The apparatus consists of the mould, the reservoir, and a communicating passage or attachment arranged between them. The three parts may be formed separately from each other as shown, or the mould and connecting passage may be integrated and the reservoir firmly joined to the passage, or the reservoir and passage may be integrated and the mould firmly fastened to the passage, or the three parts may be all integrally attached.

The relative arrangement of the three members is such that, along an internal edge, they form a straight continuous line when connected together. The sectional form of the attachment is essentially the same as that of the adjacent portions of the mould and reservoir; but its peripheral dimensions are only about two-thirds those of the mould. The connecting passage and reservoir are provided with a lining of fireproof material.

The molten metal is first introduced into the reservoir, when the apparatus is in position 1, in which reservoir the metal may be further prepared for the actual casting process. Casting is effected by tilting the apparatus through an angle of about 180°, whereby the liquid metal passes from the reservoir into the mould.

The successive positions 2–6 are taken up by the apparatus during the operation of tilting. As will be understood, the liquid metal retains its horizontal surface in all positions and there is merely a gradual change in the position of the metallic liquid from the reservoir to the

mould, until, finally, the metallic liquid takes up the position 6 inside the mould, and is there able to solidify into the form of an ingot. During the passage of the metallic liquid from the reservoir into the mould no throttling or damming-up occurs in the connecting channel or attachment, and therefore, in spite of the rapidity with which the apparatus can be turned over, the transference proceeds in a perfectly quiet and uniform manner. No intermingling of the liquid metal with air, slag or other oxidizing particles can occur during this operation.

The essential features of the Durville process are contained in Claim 1 of the specification : " An improved process of casting ingots of metals and alloys which consists in first introducing the molten metal into a reservoir arranged in alignment with the mould, and thereafter transferring said molten metal to the mould, without pouring, by tilting the apparatus in such a manner that the surface of the liquid always remains horizontal and continuous."

The use of the Durville process made only slow progress. The British Non-Ferrous Metals Research Association performed a useful service to British industry by acquiring the patent rights for Great Britain in 1927 and making them available to its members together with a great deal of information on the practical operation of the process. By means of this process, ingots of aluminium bronze are regularly made having a surface not only free from the imperfections encountered in ingots cast by normal methods but actually superior to those obtained in bronzes not containing aluminium made by any method of pouring; in other words, the presence of aluminium in the alloy is turned from an impediment into an asset so far as surface quality is concerned.

The application of the Durville process may be illustrated by reference to one form of machine which has been evolved for the production of cylindrical ingots of aluminium bronze destined mostly for hot forging.[2] Fig. 5 (Plate XXXVI) shows the principal features of the machine used to cast ingots $3\frac{1}{2}$–9 in. in dia., up to 30 in. in length, and up to 500 lb. in weight. The mould is split longitudinally, and is provided with a refractory lining or " dozzle " at the mouth. By delaying the freezing of the metal in the head this makes the ingot self-feeding, prevents a deep central pipe and obviates the necessity for adding separate feeding metal. The addition of feeding metal, for instance from a hand ladle, is in any case undesirable because of the risk of carrying broken oxide skins down into the still molten part of the ingot. In order to assist the retention of heat in the head, a cover of refractory material, such as asbestos board, is placed on the mouth of the mould on completion of casting.

These measures to retard freezing of the head introduce an incon-

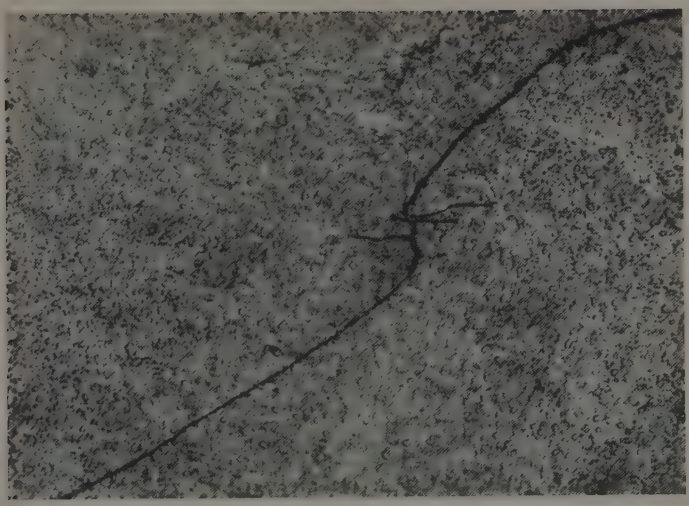

FIG. 3.—Inclusion of Oxide Film in Complex Aluminium Bronze. × 500.

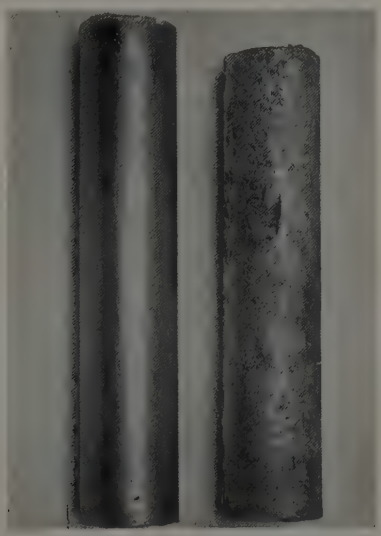

FIG. 4.—Durville-Cast Ingot (Long) and Vertically Poured Ingot (Short) of Aluminium Bronze. One-tenth actual size.

[*To face p.* 332.

FIG. 5.—Durville Casting Machine.

venience in production, which becomes serious when it is important to maintain the maximum output from a foundry. Unless special steps are taken it is necessary to leave the mould on the machine until the head has solidified, the usual procedure being then to turn the table back into the horizontal position in order to lift off the mould. In the machine illustrated this cause of delay is avoided by the provision of a simple carriage which supports the mould and can be moved outwards from the table along the pair of projecting arms. As soon as the rotary movement of the table is finished, the asbestos cover is placed on the head, the adjusting screw below the mould is turned in order to lower the mould by a fraction of an inch from the throat plate on the table, and then the carriage, bearing the mould and its ingot with the still liquid head, is rolled away from the table along the arms until it is in a position where it can be picked up by a pair of hooks suspended from an overhead hoist. The mould with its contents is then removed from the machine and placed on the floor, still in a vertical position, where it remains until the head is solidified and the mould can be stripped from the ingot. With this arrangement the output is dependent practically only on the rate at which molten metal can be delivered to the machine.

The illustration shows the robust character of the Durville machine; this is important since it is essential that there should be no unsteadiness or vibration as the mould is turned over in casting. In making a cast the molten metal is transferred, generally by hand-shanks, from the oil-fired tilting crucible furnaces to the container on the machine. The temperature in the melting furnace is so adjusted that, allowing for the cooling which occurs during transfer to the container and during the skimming operation, the metal will be at a temperature 100°–170° C. above the liquidus of the alloy, the higher temperature being adopted for the smaller ingots. There is some variation in opinion and practice in this respect: one school of thought favours a "turnover" temperature not more than 50° C. above the liquidus: this is to avoid the risk of columnar grains which are said to form at the base of the ingot if the non-turbulent metal remains molten too long in the mould. On the other hand, it is found with the complex aluminium bronzes containing nickel and iron most commonly encountered in industrial practice that the grain structure is equi-axed throughout the ingot even when relatively high pouring temperatures are employed. It may well be that the primary crystals of iron-bearing constituent ensure that there are sufficient nuclei to prevent columnar grain growth. The temperature of the cast-iron mould is 200° to 250° C., and no dressing is applied.

The metal, having been transferred to the container, is carefully

skimmed, the temperature checked as required by means of an immersion pyrometer, and rotation begun by turning the geared hand wheel. The speed of rotation is as rapid as can be conveniently achieved until the table is within about 10° of the horizontal. From this position through the horizontal to a similar angle over the other side the mould is turned slowly and carefully; it is at this stage that the surface of the metal is being greatly extended, and it is of the greatest importance not to cause a wave which would run along it into the mould and might be reflected from the base. Failure to maintain a steady continuous movement at this stage results in ripple marks on the surface of the ingot. The rotation of the table having been completed to bring it into the vertical position, the mould is removed in the manner already described.

VI.—Defects.

The defects to which inspection of Durville-cast ingots must pay special attention are:

(*a*) ripple marks and folds in the surface, caused by unsteady operation of the machine;

(*b*) patches of oxide or dross on the surface, resulting from insufficient skimming of the metal in the container;

(*c*) a central pipe, caused by pouring at too high a temperature or by attempting to cast ingots with too high a ratio of length to diameter. In the latter case the pipe tends to occur at about one-third of the way along the ingot from the base and to be displaced slightly off the central axis, away from the table;

(*d*) a fine longitudinal intercrystalline crack on the curved surface of the ingot away from the table. This defect sometimes follows an unduly high pouring temperature, particularly with a new mould having a very smooth inner surface; the crack, or fissure, is very shallow and does not show any tendency to spread during hot forging of the ingot.

The superior surface quality obtainable by the Durville process is illustrated in Fig. 4 (Plate XXXV) which shows a Durville-cast aluminium bronze ingot alongside a shorter ingot of the same alloy cast by the method normally used for brass. This is further demonstrated by the experience that Durville-cast aluminium bronze ingots can be used directly for hot forging and hot rolling without the machining which is necessary in the case of other copper-base alloys cast by the normal methods. This is naturally an important consideration from the economic point of view. On the other hand, Durville-cast ingots suffer a disadvantage in a dimensional limitation. It is very difficult

to ensure freedom from central piping when the ratio of length to diameter is greater than 8 : 1. While this is not a serious matter when ingots are intended for hot forging, nor when hot rolling is in question provided that the length is not less than 30 in. and the diameter therefore not less than 4 in., it is most inconvenient in the case of narrow ingots, say under 3 in. in dia., intended for hot or cold rolling. The inconvenience arises from the short length, less than 24 in., of these narrow ingots, which makes for great difficulty in handling at the rolls, as well as reducing the length of individual bar obtained.

VII.—Long Ingots.

When ingots of aluminium bronze having a greater length : diameter ratio than 8 : 1 are required, the general practice is to fall back on the ordinary method of pouring into a vertical mould using a single-hole tundish. The necessity has then to be faced of machining the surface of the ingot. This is objectionable not only because of the loss of value of the metal removed as turnings, but also because of the delay occasioned in the machine shops and the additional handling and transport.

P. H. G. Durville attacked this problem of securing quiet entry of molten metal into a stationary vertical mould by devising a special method of bottom-running.[3] What he calls "a sluggish flow" is brought about by pouring the metal into a vertical runner which is built up in small steps as the filling of the mould proceeds. The runner is made up of a number of elements which are placed successively one above the other in the manner illustrated in Fig. 6. The fall of the metal during the pouring is thus, at the most, equal to that of one of the elements used to form the conduit or runner.

Since the date of this patent (1922) many schemes have been developed for continuous casting, and it happens that most of these incorporate the feature of non-turbulent pouring which is so highly desirable with aluminium bronze. This applies, for instance, to those schemes where the melt is admitted to the vertical mould *via* a fin- or slot-gate, which is gradually closed by a sliding shutter rising by degrees as the level of the metal mounts in the mould. The same effect can be achieved by having the shutter fixed and causing the mould to descend at the desired rate. The authors are not aware of any published account of the use of these processes in the case of aluminium bronze.

VIII.—Control of Composition.

Reference may be made finally to aspects of technique affecting the control of chemical composition in aluminium bronzes. The normal

practice in making up the alloy is to melt the copper under charcoal, deoxidizing with cupro-manganese before adding the aluminium. For the complex bronzes, iron (as sheet clippings) and nickel (as nickel shot, cupro-nickel, or nickel-rich alloy) are charged into the crucible with the

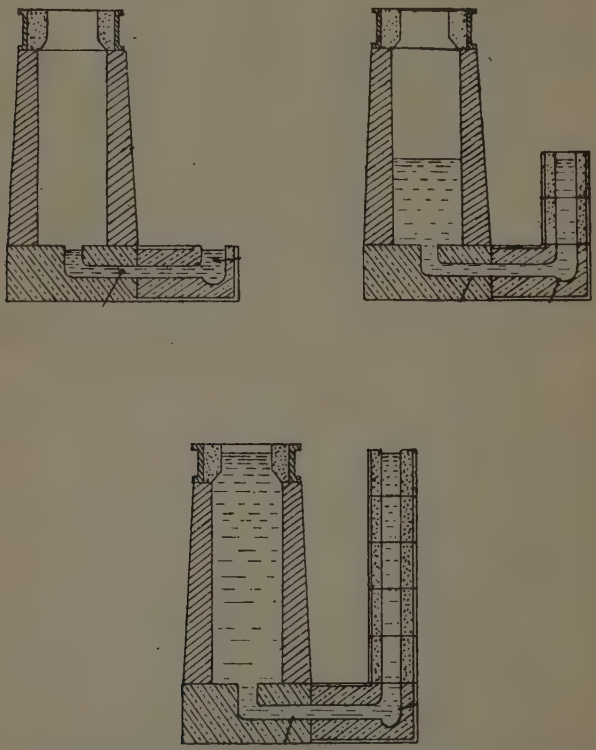

Fig. 6.—Bottom-Run Vertical Ingot with Built-Up Runner (successive stages). Reproduced by courtesy of the Controller, H.M. Stationery Office, from British Patent Specification No. 178,091 of 1922.

solid copper. When all the iron and nickel have been dissolved, a proportion of the copper ingot, held back from the initial charge, is added in order to reduce the temperature of the melt before incorporating the aluminium. Thorough mixing is ensured by the use of a plumbago plunger applied with an up-and-down movement.

Special attention is directed to the mixing of the aluminium because the mechanical properties are quite sensitive to variations in the concentration of this component. Moreover, it has to be remembered that when present to the extent of 10 wt.-%, the aluminium constitutes about 30 vol.-% of the charge, and on account of its low density it tends to remain on top of the melt until it is driven down by the plunger.

As a supplement to the routine chemical analysis of casts, a small finger sample taken from the crucible and fractured in the melting shop gives a useful check, at least in the case of the complex forging alloys. A comparison of the appearance of the fracture with that of standard analysed bars gives surprisingly accurate results in the hands of an experienced man. With this class of aluminium bronzes also, regularity of composition throughout the products of a melt can be checked very effectively and promptly by making a Brinell hardness test on each ingot. For each composition it is possible to specify upper and lower limits for acceptance. These limits have to be related, naturally, to the size of ingot, but they are not highly sensitive to this factor: the same range is applicable, for example, to ingots of 3 in. and 6 in. dia.

IX.—Summary.

Aluminium bronzes are characterized by a short freezing range, not exceeding 15° C., accentuating the tendency for deep central piping in cylindrical ingots. The oxide film which forms on molten aluminium bronze greatly impedes the absorption of furnace gases. The use of fluoride-containing fluxes is undesirable because by removing the oxide film they permit the entry of gas into the melt, with increased risk of pin-hole porosity in the ingot.

The tenacious film of oxide on the molten metal is also the decisive factor as regards the surface quality of the ingots. When casting is effected by special non-turbulent methods the oxide film assists in producing a very smooth skin on the ingot. The Durville process achieves this by an arrangement in which the container for the molten charge and the ingot mould are connected together on a table which is rotated so as to displace the metal from the container to the mould without breaking the surface.

The industrial application of the Durville process requires a robust machine to ensure steadiness of operation. Handling devices may be incorporated in the machine for avoiding delay due to the slow solidification of a feeding head. Defects in Durville-cast ingots may arise from unsteady operation, insufficient skimming of the metal in the container, incorrect casting temperature, or excessive ratio of length to diameter.

The Durville process is not suitable for ingots of aluminium bronze having a length : diameter ratio greater than 8 : 1. In such cases vertical casting has to be used, with adverse effect on surface quality. Improvement may be achieved by special methods of casting which avoid excessive fall of the metal in pouring; continuous casting may be applicable.

Accurate control of aluminium content is important in bronzes in the range of composition used for hot forging. Hardness tests provide a rapid check to supplement chemical analysis.

ACKNOWLEDGEMENTS.

The authors wish to thank Messrs. J. Stone and Co., Ltd., for permission to reproduce illustrations of processes used and products made at their Charlton Works. They are grateful also to a number of their colleagues, and especially to Mr. E. F. Hodges, A.I.M., and Mr. A. R. H. French, A.I.M., for assistance in preparing this paper. Fig. 1 is reproduced by permission of the American Society for Metals, Fig. 3 by permission of the British Non-Ferrous Metals Research Association, and Fig. 6 by permission of the Controller of H.M. Stationery Office, to all of whom grateful acknowledgement is made.

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THE APPLICATION OF FLUX DEGASSING TO COMMERCIALLY CAST PHOSPHOR BRONZE.* 1159

By N. I. BOND-WILLIAMS,† B.Sc., A.I.M., Member.

Synopsis.

This paper describes the application of the principles of good melting and casting practice discovered in the past by various workers, and reported in papers to the Institute of Metals and other societies. The particular application considered is to the melting and casting of phosphor bronze for subsequent cold rolling. Improvement in properties and economy are found to result from flux degassing, slow pouring, the reduction of agitation, and alterations to mould design.

I.—Introduction.

Changes in established industrial practices, particularly in the older trades, often take place slowly; growth and development are almost organic, and frequently the credit that is due to fundamental scientific work in this process becomes obscured and consequently is belittled or ignored altogether. The object of this paper is to show that certain changes made in the practice of melting and casting bronzes in a British factory have their origin in published scientific work that preceded them, summarized in the paper " The Melting and Casting of Non-Ferrous Metals ", by G. L. Bailey and W. A. Baker.[1]

The changes and the reasons for them are best described and illustrated by contrasting the practice before the application of these scientific principles, and at its present stage of development. The period taken to make all the changes described was approximately ten years. The final product was the same throughout the period, namely, chill-cast phosphor-bronze slabs and wire bars intended for rolling into strip and rod.

II.—Requirements of the Product.

These chill castings must be suitable for cold rolling. To be suitable, they must satisfy not only technical requirements, but must also be produced at low cost and fulfil the demands made by commercial management. The requirements may be summarized as technical, economic, and commercial.

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1. *Technical.*

The technical requirements are :

(a) *Consistency of size and shape to allow for standard rolling schedules.*

Castings that vary in size or shape need preliminary rolling to bring them into condition for a series of standard rolling reductions. Not only do these correcting passes cause excess costs, but they also cause secondary problems. Light correcting passes may give rise to fire-cracking if the slabs are annealed before starting the standard rolling schedule; if the slabs are not annealed, these light passes will vary the amount of cold reduction within the batch and will consequently cause cracking through over-work. Slabs that are annealed successfully after light correcting reductions will possess different microstructures from those that have not needed correction, and may exhibit very different physical properties throughout rolling.

(b) *Consistency of physical and chemical properties to permit standard thermal processes.*

Variations in composition and structure of the castings that affect the response of the material to heat-treatment, i.e. to the initial high-temperature soaking to destroy the cored cast structure and to subsequent annealing treatments after cold rolling, will lead to increased costs for special treatment. They may also cause the dimensions of the rolled product to vary, and so upset standard rolling schedules and even the accuracy of the finished product, either by variation of dimensions or of hardness and strength.

(c) *Good surface quality* and the elimination of cold shuts, spills, oxide films, folds and inclusions, cracks, exuded layers, and spots.

(d) *Internal soundness*, and freedom from gas and contraction cavities, entrapped air, cracks, and non-metallic inclusions.

2. *Economic.*

The economic requirements are :

(a) *Technical consistency of the process* and the product.

(b) *Economy in the use of fuel*, additives, fluxes, crucibles, and special apparatus.

(c) *Long life of moulds.*

(d) *Minimum unavoidable process scrap*, both from casting and subsequent operations.

(e) *Minimum unavoidable metal loss in casting.*

3. *Commercial.*

The commercial requirements are:

(a) *Flexibility of the process to suit variations in demand for quantity and size.*

The market that is available for phosphor-bronze strip and rod is limited in volume to orders for small quantities seldom exceeding 1 ton of a single size, and frequently the final use calls for specially heavy coils. The popular method of casting standard-width strips and subsequently slitting to various widths, does not fulfil the demands of the market.

(b) *Consistency of quality.*
(c) *Consistency of output.*
(d) *Suitability for available plant and labour force.*
(e) *Suitability for available raw materials.*

Throughout the ten-year period, the range of sizes ultimately required from the rolling mill was unaltered: strip from 3 to 12 in. in width and 0·010 to 0·125 in. in thickness, and rods from $\frac{1}{4}$ to 1 in. dia. The number of alloys required increased from two main alloys, containing 3 and 5% tin, to various alloys ranging from 2 to 12% tin. In every case, the phosphorus content was approximately constant at 0·15–0·2%, the normal residue after deoxidation of the melt.

III.—Materials Available.

The available raw materials for melting were the same throughout: electrolytic and fire-refined H.C. copper as process scrap from the factory's copper mill, high-purity tin of various brands (principally Mellanear, Lamb and Flag, and Chempur), tin-bronze process scrap from the rolling mill, and commercial high-grade phosphor copper containing 15% phosphorus.

IV.—The Original Process.

1. *Plant and Technique.*

The furnaces were the normal type of natural-draught coke-fired pit furnaces. Eighteen furnaces were arranged in line on a common horizontal flue. This flue was connected at each end and at the centre with a main flue, also horizontal, and parallel to the first. The main flue was connected at one end to a brick chimney stack 70 ft. high and $4\frac{1}{2}$ ft. dia. The chimney stack was not connected to any other furnaces. The furnaces were large enough to contain a standard 160-lb.-capacity

crucible, and with the bottom of the crucible resting on the fire-bars the lip was level with the bottom of the rectangular flue opening and about 16 in. below the lid. The flue opening was approximately 9 in. long by 7 in. high. The grate was made of square-section fire-bars $1\frac{1}{2}$ in. thick and spaced $1\frac{1}{2}$ in. apart. Below the grate was a clear vertical space of 3 ft. at the side of a tunnel 6 ft. high by 4 ft. wide, which led directly outside the building, admitting air to the furnaces with the normal outdoor temperature and humidity.

The 160-lb. salamander crucible, after warming, was placed on a split firebrick resting in the centre of the fire-bars and surrounded by a low fire. The furnace was then filled with coke-oven coke, graded $1\frac{1}{2}$–2 in., up to the level of the lip of the crucible, and the lid closed until the crucible was well heated and the whole fire burning brightly. The copper process scrap and phosphor-bronze scrap were charged on top of a layer of stick charcoal, and liberally sprinkled, after charging, with powdered charcoal. The fire was rammed down with an iron poker, and a further quantity of coke added. The lid was then closed until the metal was molten and reached the desired temperature. This was estimated by the pourer, and generally took between $1\frac{1}{4}$ and $1\frac{1}{2}$ hr., although on occasions a charge was known to take a full 2 hr. to melt. Sometimes it was necessary to add a further quantity of coke during melting.

When the melt reached the desired temperature, the pourer skimmed off the larger lumps of charcoal from the surface of the metal, and added the phosphor copper to the charge while it was still in the furnace. After stirring in the phosphor copper with a salamander stirring stick, the pourer added the tin, stirred, and withdrew the crucible. After manœuvring the crucible into position at the end of a row of moulds, the pourer skimmed off any dross and remaining charcoal and poured the metal into the mould or moulds. While pouring, the lip of the crucible was rested on the edge of the back half of the mould, and then tilted until a steady stream of metal was projected down to the bottom of the sloping mould.

The mould had previously been warmed slightly and dressed with a heavy coat of seal oil to which had been added powdered French chalk and powdered charcoal. The dressing was heated to expel water and then applied with a brush. The mouth of the mould was open; there was no tundish or funnel to control the pouring stream. The size of the strip moulds varied in width from 3 to 12 in. and in thickness from 1 to $1\frac{1}{4}$ in. They were cast with thin walls and rebates, and closed with two rectangular rings and wedges. The wire bars were $1\frac{5}{8}$ in. square × 5 ft. long, and were closed with three rings and wedges.

2. *Results of Casting by the Original Method.*

(a) *Consistency of size and shape.*

There was a tendency for the centre of the long sides of the slabs to contract, resulting in a slight concavity. When subsequently rolled, this was the cause of cracking, owing to unequal elongation of the longitudinal sections of the casting.

(b) *Consistency of physical and chemical properties.*

The physical properties varied considerably, particularly ultimate tensile strength and elongation, on account of unsoundness and variable distribution of porosity and inclusions. In addition, the tin-rich second phase in alloys containing more than 5% tin, was very difficult to remove by prolonged heat-treatment, probably on account of microporosity interfering with diffusion.

(c) *Surface quality.*

Surface quality at first sight was very good. The smooth blue-grey surface, free from blemishes, seemed excellent, but proved to be a layer of "tin sweat" of considerable thickness (see Fig. 5(*b*), Plate XXXVII). When rolled, this broke into flakes, giving the strip a final appearance similar to a coarse-grained wood. This defect could only be removed by machining away $\frac{1}{8}$ in. from each flat surface of the cast slabs. While present, the tin sweat masked other surface defects, and its removal served the double purpose of removing the cold shuts, spills, surface gas cavities, and spots.

(d) *Internal soundness.*

Internal soundness was shown to be poor by physical tests and also by the difficulty experienced in diffusing the tin-rich second phase in the higher-tin alloys. Specific-gravity measurements confirmed this fault, but its ultimate effect on the final rolled product was less serious than the surface imperfections. It is assumed that many of the small discontinuities within the casting were pressure-welded in the rolling process.

(e) *Consistency of the process and product.*

The process was consistent in its results, and repeated castings showed stable costs, although these costs were high on account of the large amount of process scrap involved in machining, and a proportion of rejects for excessive internal unsoundness and cracking during rolling. The product was not consistent enough in its physical or chemical properties to be suitable for the close scrutiny applied by consumers using precision mass-production methods. This led to excess costs in

selection of material from finished batches to comply with consumers' demands.

3. *General Considerations.*

(a) *Economy in the use of fuel, &c.*

(i) *Fuel.* The slow rate of melting and the bad grate design caused fuel consumption to be unnecessarily high. The consumption was about 10 cwt. of coke per ton of metal melted.

(ii) *Additives, fluxes, &c.* The cost was low. Apart from the necessary metals and alloys, only a small amount of charcoal was used.

(iii) *Crucible life* was good. There was little or no erosion, and as many as 50 heats were frequently obtained from standard crucibles.

(iv) *Special apparatus.* There was no cost.

(b) *Life of moulds.*

The life of the cast iron moulds was shortened by the impingement of the molten metal on the walls, owing to the lack of control, other than the pourer's skill, over the stream of molten metal. This led to crazy cracking of the mould surfaces, followed by surface gassing of the casting, and finally to break-up of the moulds.

(c) *Process scrap.*

This was considerable, as not only was it necessary to machine away nearly 20% of the casting to remove tin sweat, but also the excess shrinkage caused by rapid pouring gave rise to deep sinks and the need for cutting off long gate ends. Internal unsoundness led to further process scrap being made while rolling.

(d) *Metal loss.*

Casting and melting losses were low.

(e) *Flexibility.*

The process was flexible for size and quantity, but limited for the range of alloys. It was difficult to produce alloys containing much more than 6% tin in suitable condition for cold rolling.

(f) *Consistency of output.*

Output could be forecast with fair confidence, but process scrap seemed excessive, and limited the maximum output.

(g) *Suitability for plant and labour.*

The process was suitable for the equipment, but the standard of skill demanded from the pourer was very high, and the available labour force consequently small and diminishing.

(h) *Suitability for raw materials.*

No difficulty was met in using the available raw materials, although the recirculating process scrap was higher than desirable on account of machining and other avoidable process scrap.

V.—The Modified Process.

Flexibility was the main advantage of the original process, and as it seemed particularly suited to the market available for rolled or drawn

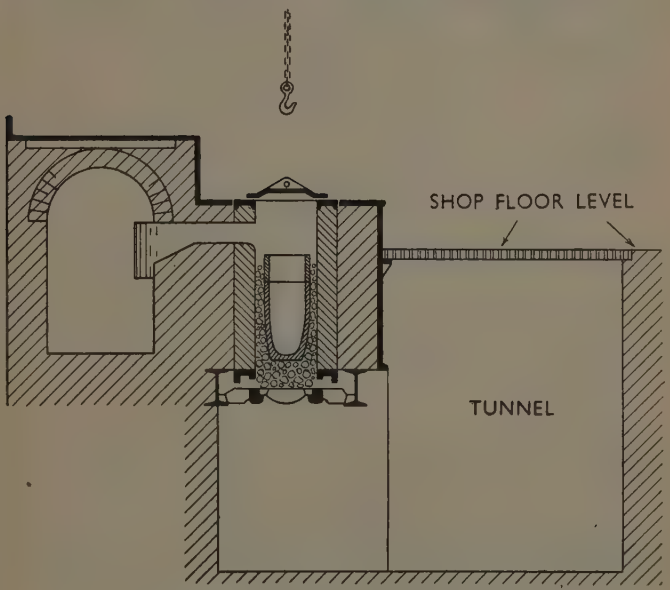


Fig. 1.—General Arrangement of Modified Furnace.

tin bronze, modifications were gradually made to eliminate some of the apparent disadvantages of the original process. It would not be possible to describe these in chronological order without fear of inaccuracy, or confusion in the mind of the reader, so the modifications to the elements of the process will be described in the same order as in Section IV.

1. *Furnaces.*

The furnaces were rebuilt completely in order to reduce melting time and fuel consumption, and to provide a strongly oxidizing atmosphere

(Fig. 1). A patented design of grate (Wigley) was used in a furnace of approximately the same internal dimensions as before. The grate was arranged to support the body of the fire on two small combined fire-bar castings assembled into a massive cast-iron frame. On each of the four sides of this frame a large oblique rectangular opening was provided which admitted air to the level of the top of the fire-bars, both for combustion of the coke and also to cool the grate. The fire-bars themselves had narrow gaps approximately $\frac{1}{2}$ in. wide, which only permitted ashes of completely burned coke to fall into the ash pit (Fig. 2).

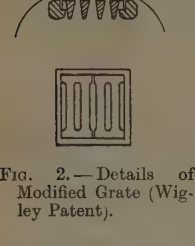


FIG. 2.—Details of Modified Grate (Wigley Patent).

The furnace flues and flue openings into the main horizontal flue were redesigned to permit a streamlined flow of the products of combustion and to provide an extractor effect at each flue opening. The second horizontal flue was eliminated, and the new streamlined flue connected at one end direct to the original chimney stack. The effect of these alterations, together with improved refractory insulation, brought down the melting time to 45 min., and the coke consumption to approximately $4\frac{1}{2}$ cwt./ton of metal melted. The charge could be melted with only one supply of coke, and it was not necessary to open the furnace lid, except for inspection, until the melt was up to temperature.

2. *Slag Treatment.*

Before charging the metal, a slag is prepared in the crucible by introducing equal weights of dry sand, copper mill scale (CuO), and fused borax. This slag should equal at least 3% by weight of the charge. When the charge reaches a temperature of 1250° C., the slag is drawn to one side and the tin added while the crucible is still in the furnace. The charge is stirred vigorously with a salamander rod, and the crucible is then withdrawn from the furnace and placed in a tilting cradle. Dry sand is added to the slag to thicken it, and the slag is skimmed off. The phosphor copper is added, and stirred thoroughly. When the reaction is complete and the temperature of the charge falls to 1200°–1250° C., the metal is poured.

The tilting cradle is arranged on rails parallel to the line of moulds, and is so designed that by pulling a lever the crucible is tilted on the axis of its lip. The lever can be operated by one hand of the pourer, leaving the other hand free to use a skimmer if necessary (Fig. 3).

Each of the moulds is hung vertically on a steel framework. Mounted on trunnions at the top of each mould is a tundish arranged

with holes to direct a controlled stream of metal vertically down to the bottom of the mould. The moulds are book-type, cast iron, and closed with C-clips fitting over wedge-shaped projections on the mould doors. The tundishes and moulds are in such relation to the cradle and crucible that the lip of the crucible is above the edge of the tundish, and the metal is poured quite rapidly without splashing until the tundish is

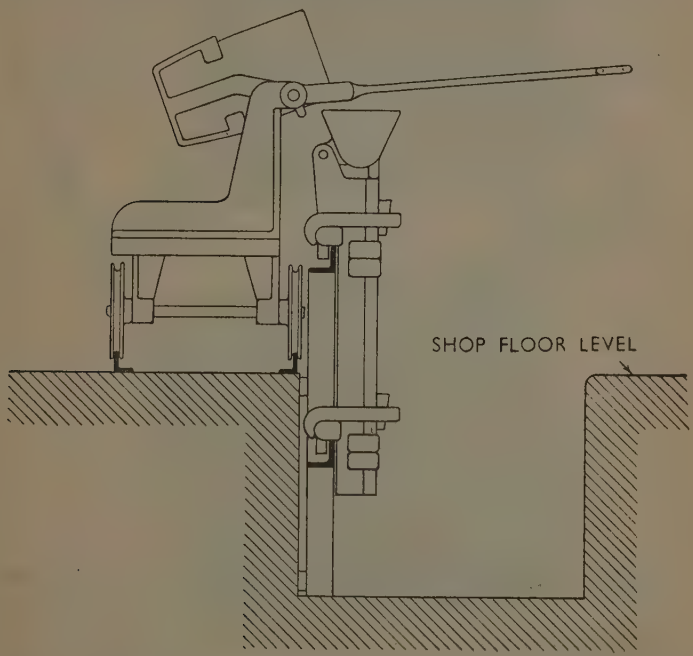


FIG. 3.—General Arrangement of Modified Pouring Cradle, Tundish, and Mould.

nearly full. The rate of pouring is then reduced to maintain a constant level of metal in the tundish. The rate of flow of metal into the mould is regulated by the size of hole in the tundish.

The size and number of holes is varied to suit the width of different moulds. Turbulence within the mould, impingement, and local overheating of the mould are all avoided or reduced by the use of a number of small holes in preference to one larger one, and distribution and feeding of metal in a wide mould are improved. The holes are designed to reduce the pouring rate to approximately one-sixth or less of the unrestricted

rate of the earlier practice. For example, the time taken to fill a mould $2\frac{1}{2}$ in. square and 38 in. long is 120 sec., compared with 15 sec. or less in the earlier practice.

The tundish design is worthy of special mention (Fig. 4). Originally used for brasses, they were made of iron castings of heavy section, with holes of moderate size, and were found quite successful. The very low pouring speeds demanded for casting sound bronze called for much smaller holes, and it was soon found to be impossible to pour any appreciable quantity of metal through these holes in a casting of 1 in. section, even if the tundishes were heated to a dull red before pouring.

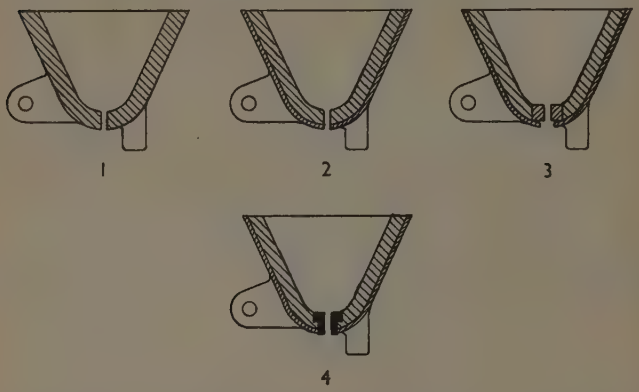
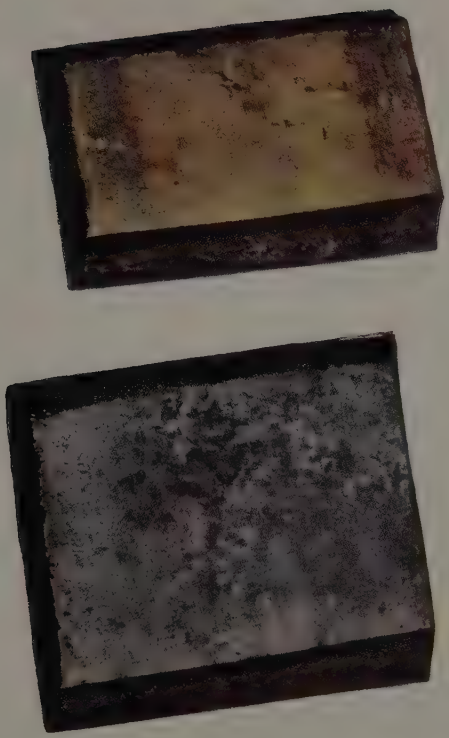


FIG. 4.—Development of Tundish.

1.—Solid cast iron; 2.—steel with rammed fireclay lining; 3.—steel with fireclay lining and firebrick insert; 4.—steel with fireclay lining and graphite insert.

A light steel-sheet tundish was made and lined with fireclay to overcome this difficulty, and was successful, but it had a very short life. The important feature of the tundish hole is that it should direct a single smooth stream directly to the bottom of the mould. In the steel-sheet tundish, the lower edge of the hole in the fireclay lining was moulded round a steel pattern and was easily chipped after being used once or twice. If the edge of the hole is chipped, the stream will be deflected and sometimes broken into two or more streams or a series of drops.

The second alternative was to line the bottom of the tundish with a segment made from a close-textured firebrick into which a suitable hole had been drilled, building up the remainder with fireclay. This tundish had a longer life, but failed in the same way as the other. In both



(*a*)

(*b*)

FIG. 5.—Two Sections of Cast Strip Ingots as Removed from the Mould Without Subsequent Treatment. One ingot (*a*) shows a typical cast bronze colour without tin sweat. The other (*b*), cast by the old method, shows a uniform heavy layer of blue-grey tin sweat.

[*To face p.* 348.

cases it was necessary to scrap the whole lining when the hole was damaged.

Finally, a design was tried making use of a turned graphite bush, fitted into a pre-cast fireclay lining. This was found to be quite satisfactory as it had a long life, did not fail by chipping, but by gradual opening of the hole, and was easy to replace without destroying the entire lining. Graphite possesses the additional merit of not being wetted by molten bronze, and consequently this tundish did not suffer, as do other types, from solidification of the last drops of bronze in the hole.

The moulds are warmed slightly before use, and are dressed with a volatile oil with no solid addition. The dressing is very sparsely applied, and then any excess is rubbed off with a rag. Particular care is necessary to avoid a pool of oil forming in the bottom of the mould.

The mould sizes were also altered, partly to increase the weight of the castings for commercial reasons, but mainly to make it easier to avoid impingement of the metal stream on the mould faces. The strip moulds were increased to $1\frac{1}{2}$ in. thick, and the wire bars to $2\frac{1}{2}$ in. square. At the same time, the moulds were re-designed to have a massive bottom, increasing the heat content of the mould at this point, in order to encourage solidification from the bottom.

3. *Results of Casting by the Modified Method.*

(a) *Consistency of size and shape.*

The tendency for concavity of the flat sides is reduced. The slow rate of pouring and the changes in mould design encourage solidification from the bottom of the mould, and reduce the depth of the zone of partially solidified and liquid metal. The flatter isotherms that result in the partly solidified or pasty zone reduce the tendency for a deep central shrinkage cavity, and permit the shallow pool of liquid metal to feed the distributed shrinkage cavities as they are formed. Lateral shrinkage is avoided and the casting is of much improved shape.

(b) *Consistency of physical and chemical properties.*

These properties are both improved and more regular. Owing to the reduction in unsoundness, no difficulty is found in absorbing the tin-rich constituent into solid solution by subsequent heat-treatment.

(c) *Surface quality.*

Tin sweat is completely avoided, and provided that mould surfaces are good no other blemishes are found to any considerable extent (see Fig. 5(*a*), Plate XXXVII). As mentioned above, solidification takes place

mainly in one direction, and segregation is reduced. The tin-rich phase does not occur in such large areas, and by reason of the reduction of lateral shrinkage, it is not exuded between the cored crystals into the space between the surface of the casting and the mould. Internal gas pressure is reduced by the degassing process, and this also reduces the tendency for exudation. Strips cast in this way are rolled without machining.

(d) *Internal soundness.*

Internal soundness is improved, as shown by specific-gravity determinations.

(e) *Consistency of process and product.*

The process is consistent and the process scrap much reduced, both at the casting stage and in subsequent working and treatment. The product is more consistent, and selection is not normally necessary.

4. *General Considerations.*

(a) *Economy in the use of fuel, &c.*

(i) *Fuel.* Furnace reconstruction led to a very large reduction in fuel consumption and melting time.

(ii) *Additives, fluxes, &c.* This is an additional cost compared with the original process, but the materials used are all cheap, copper mill-scale being a by-product of another factory process.

(iii) *Crucible life* is reduced slightly by slagging action, but this does not cause a serious increase in cost. Crucibles still give up to 38 heats.

(iv) *Special apparatus.* Under this heading, the only recurring cost is the repair of tundishes. This is a small item.

(b) *Life of moulds.*

Pouring vertically at controlled speeds lengthens the life of moulds considerably. The first cost of book-type moulds is higher, but is more than covered by the increased life.

(c) *Process scrap.*

Slow pouring and regulated solidification yield a casting with a very small sink. Generally, this does not exceed $\frac{1}{2}$ in., and this reduces the need for cutting off substantial gate ends. Machining of tin sweat is eliminated and subsequent process scrap reduced.

(d) *Metal loss.*

Melting losses are increased slightly on account of entrapped metal in slag and absorption by tundish linings. This increase is not significant.

(e) *Flexibility.*

The modifications do not impair the flexibility of the process. It still permits a wide range of alloys and sizes to be made.

(f) *Consistency of output.*

Output is consistent, and reduction of process scrap permits of a net increase in rolled-metal output.

(g) *Suitability for plant and labour.*

The plant required is almost the same as before. The demand on skill in the case of the pourer is reduced by the cradle and tundish arrangement, and lower-quality labour may be used if fully skilled men are not available.

(h) *Suitability for raw material.*

No difficulty is found. The improvement in physical properties permits a reduction in the tin content, if this is permitted by the specification, with consequent reduction in cost. Recirculating process scrap is reduced, although excellent results have been obtained with sample heats consisting entirely of scrap.

VI.—Origin of Changes.

From a comparison of the results of the original and the modified processes, there can be no doubt that there has been, over a period of 10 years, a considerable improvement in technical properties, costs, and commercial advantages. No single discovery is claimed to be responsible for this but only the diligent application of principles already well known, and published by the learned societies and research institutions. Bailey and Baker, in their paper,[1] have analysed these into headings, and many of these headings can be compared directly with this example of factory practice. Briefly they are :

(1) " A clean stream of metal must be poured ". Freedom from dissolved gases is dealt with below in detail. Particles of slag, fuel, and other solids that may have accumulated on the surface of the melt in the furnace are almost entirely removed with the thickened oxidizing flux, and any small quantity remaining is effectively removed in the pouring tundish, as the pouring stream flows from the bottom of a deep pool of metal.

(2) " The stream must remain clean ". This is ensured by a deliberate excess of the deoxidant, phosphorus, and the use of a thin coating of flaming-oil dressing on the mould.

(3) " The stream should be poured in a tranquil manner ". After

stirring of the charge is complete, agitation is carefully avoided by the combination of pouring cradle, tundish, and vertical mould.

(4) " It must be poured at a sufficiently high temperature ". The cradle arrangement reduces the discomfort to the pourer of working close to crucibles containing charges at high temperature. The tundish design reduces heat loss and fall of temperature during pouring,

(5) " The lightest stream that can be conveniently used ". The tundish hole restricts the size of the pouring stream. Small streams are used, and in the case of wide moulds, more than one hole.

(6) " Reduction of the over-all pouring rate ". This is achieved by the tundish control. The pouring rate was determined by experiment to be the slowest rate still avoiding the formation of cold shuts.

(7) " Avoidance of injection of air bubbles ". The pouring stream from the tundish is arranged to be as small as possible and the shape of the stream smooth. Vertical moulds permit any entrapped air to escape without collecting beneath one face of the mould, as would be the case if sloping moulds were used.

(8) " Removal of dissolved gases—by increase in oxygen content ". The oxygen content of the charge is increased by the use of an active oxidizing flux, by avoiding the production of excessively reducing conditions in the furnace atmosphere, and by removing reducing materials (i.e. charcoal) from contact with the melt.

(9) " Removal of dissolved gases—removal of excess oxygen ". When there is no serious danger of further absorption of reducing gases the oxygen is removed by addition of phosphorus.

(10) " Residual deoxidant is desirable ". A deliberate excess of phosphorus is left in the charge to protect the stream and the molten urface of the metal in the mould.

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REFERENCE.

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THE MELTING AND CASTING OF BRASS.* 1160

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SYNOPSIS.

Taking the word brass to cover binary alloys of copper with 20–45% zinc, as well as more complex alloys resulting from the addition of one or more other elements in much smaller proportions, a review is made of the most important features of brass-melting practices, especially those of metallurgical interest. After indicating the requirements regarding quality and the significance of composition in the production of castings for subsequent fabrication, the suitability of different types of melting units used is briefly discussed. In considering the melting process, possible sources of contamination, means of minimizing metal loss due to oxidation, and the addition of other elements are described. As moulds and mould dressings feature importantly in the technology of brass production, various aspects of these are examined in some detail with reference to their effect on the quality of the product.

The conditions under which the transference of molten metal into the mould is made, that is, the actual process of pouring or casting, involve both mechanical and metallurgical factors, and these, together with the process of solidification, and their effect on it, are broadly considered.

I.—INTRODUCTION.

THE word brass is usually understood to mean an alloy of copper and zinc containing not less than about 20% and up to about 43% zinc. It is used in referring both to binary alloys of these two metals and to more complex copper–zinc alloys containing smaller amounts of other elements introduced to impart special properties, but consideration of one major group, the nickel silvers, is omitted since these are dealt with elsewhere in this Symposium. The purpose of the present paper is to outline some of the most important features of brass-melting practices, especially those of metallurgical interest and significance. So considerable is the amount of detail and information existing that only the broadest outline can be attempted in a single paper dealing with the subject as a whole.

The shapes cast for subsequent fabrication, that is, ingots, billets, and slabs, with which this paper is concerned, vary in weight from a few-score pounds to several tons, the largest being in those alloys which are processed by hot rolling. With such diversity of composition, size,

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and shape, there are consequently many differences in established production techniques, but the chief metallurgical considerations involved in melting and casting the whole range of alloys are essentially similar, because of their content of zinc, which has a high vapour pressure at temperatures of the molten alloys.

A satisfactory casting might be defined as one which is compositionally correct and which on processing by the appropriate techniques yields an acceptably high proportion of marketable material. Its surface, therefore, must be substantially free from blemishes such as pits, folds, cold shuts, trapped oxide, or foreign matter, &c., or capable of being so treated that any such defects can be readily and economically removed either before or during processing. Internally the casting should be sound, that is, as free as possible from shrinkage cavities, blow-holes, gas pores, or other discontinuities, since these cannot usually be eliminated and so tend to persist as defects in the finished product, be it plate, sheet, strip, rod, tube, or wire. The structure of the ingot or billet must be such that there is no inherent weakness such as unsuitable crystalline configuration, segregation, or cracking, to give rise to failure in subsequent processing. Finally, the shape of the casting should be that most suited, from all points of view, to the process or processes to be followed in its fabrication.

Many thousands of tons of chill-cast brass shapes are produced every week and a high standard of quality is reached and maintained as a normal everyday matter. The fact that the production of high-quality shapes substantially free from defects is not always universally and consistently realized, however, is not because of any serious technical difficulties in the processes or unsolved major metallurgical problems, since, in general, for most of the alloys in this category these no longer exist. Failure, therefore, to produce castings of satisfactory quality must be ascribable to an ignorance of, or a lack in the application of, the knowledge derived from long practical experience and specific investigations. With few exceptions brass alloys are easier to produce, in the form of chill-cast shapes, than aluminium bronzes, tin bronzes, or silicon bronzes, or, indeed, any other major group of copper-base alloys, and by the use of techniques based on available metallurgical knowledge it is not a difficult matter to manufacture regularly and in quantity good-quality products.

II.—Make-up of Charge.

To ensure that the resulting casting is of the composition required, the utmost care is necessary in the selection and weighing of all raw materials, scrap, temper alloys, &c. The two main virgin metals used,

copper and zinc, are available in high purity, and the small amounts of the impurities which are present are not deleterious in their effect on the alloys. The other elements which are added, usually in alloy form, in making ternary and more complex brasses, are also obtainable in a relatively high degree of purity. Using such materials and observing the necessary precautions in melting and casting, it is possible to produce brass alloys accurately to defined compositional limits with low impurity content. For reasons of economy, as in the production of other metallurgical materials, scrap is used to a considerable extent. When this is limited to process scrap, that is, ingot ends, shearings, slittings, &c., the risk of increasing impurities is but slight. On the other hand, the use of scrap from outside sources is a potential source of trouble so far as composition is concerned, and should not be adopted without analytical check and control.

The control of composition is not only necessary to ensure that the alloy complies with the requirements of the specification it may have to meet, but it is important in regard to fabricating operations. This may best be illustrated by reference to lead in alpha brass. In alloys of this type, when lead is not specifically required, and therefore not added as an alloying element, specifications quite commonly admit of amounts up to about 0·07% since this quantity has no appreciable effect on the general properties of the alloy. Such material can be cold rolled from the ingot, indeed alpha-brass alloys such as the so-called engraving brasses containing as much as 1% and more of lead can be cold rolled without edge or surface cracking, but for successful hot rolling the lead content must be strictly limited to less than 0·02%. Thus within the limits allowed by a specification the composition can be all-important in determining the suitability or otherwise of the material for particular fabricating processes. Again, the presence of iron is beneficial in reducing the tendency of leaded alpha–beta brasses to crack on hot rolling. Many more could be added to these examples illustrating the effect of composition, and, therefore, the importance of adequately controlling it, so far as manufacturing processes are concerned, but they must suffice to illustrate this point since the paper is not primarily concerned with the effect of impurities or added elements.

Less is heard now than formerly regarding the relative merits of heats made up wholly from virgin metals and those in which scrap metal is incorporated. More is known of the gas content of virgin and other metals and ways and means of dealing with it. More too is known of the effect of other elements not only on the physical and mechanical properties of the alloy but in the melting and casting processes, and

there is, therefore, really no issue, for satisfactory products can be made from either, provided that in doing so full use is made of existing metallurgical knowledge.

III.—Melting Units.

A wide variety of types and sizes of furnaces has been, and is, used for melting brass alloys for casting into shapes for subsequent fabrication. From strictly metallurgical considerations, that is, in particular, the quality of the resulting product, there is, perhaps, little to choose between them provided that the melting operations are carried out with that degree of care and precision in control which such a fundamentally important process as melting requires, since the alloys are not, in general, sensitive to gas pick-up, nor, again in general, do they suffer much more than loss of zinc by oxidation. The considerations, therefore, which determine the choice of melting unit are usually and largely other than metallurgical and are, in fact, more related to economics, type and quantity of production, availability of fuels, and the like.

It will be quite clear that where the production of an alloy of any particular composition is not more or less continuous and is small both in regard to tonnage and size of individual castings, units of a discontinuous kind, that is, where the individual charge is completely emptied in casting, would normally commend themselves. Such units include solid-, liquid-, or gaseous-fuel crucible furnaces of the lift-out or tilting variety, or electric-arc furnaces. Where tonnage and individual castings are large, but of various compositions, the melting capacity may well consist of an aggregate of small units, or correspondingly large discontinuous units may be preferred such as the reverberatory, electric resistance, or arc furnaces. For large outputs where changes in composition are not frequently made and are not of a major kind, that is, where the production of a particular composition can be considered as continuous, the low-frequency induction furnace has an established place and in these circumstances is generally used. While it may be reasonably inferred from the extent to which furnaces of this type have been increasingly employed in the last few years, that they may be the most suitable so far developed for this type of production, all their many advantages are not and cannot be realized in other conditions, that is, where production requirements necessitate frequent changes in composition. While it is true that large quantities of brass alloys of particular compositions are used, a very wide variety of compositions in much smaller quantities is also required and, therefore, it is quite usual to find substantial capacities of the low-frequency induction type

supplemented by units of the discontinuous variety to cater for special alloys needed in greater variety but less quantity.

A detailed consideration of the relative merits of different types of brass-melting units would be much too large to include in the present paper, besides being outside its intended scope, but one or two of the more important items relating to them may be mentioned. The capacity of crucibles used in the lift-out type of furnace rarely exceeds 180 lb., and with care crucible life should be at least 80 heats. These crucibles are usually of the so-called plumbago or graphite type and to guard against premature failure they need, as indeed do all refractory receptacles for molten metal, to be preserved from thermal shock and rough usage when hot, and all types require to be seasoned and treated particularly carefully when new. Large-size crucible furnaces are usually of the tilting variety, with capacities commonly ranging from about 300 to 1500 lb., and where the metal is poured direct from the furnace into the moulds, and not into a casting ladle, the advantage of lip-axis pouring is obvious.

Although still used to some extent for brass melting, reverberatory furnaces are not often employed in the direct production of castings for subsequent working, since for a variety of reasons they are not nearly so well suited to this purpose as other types of furnace. The high-frequency type of furnace too is not used to any extent since it also has no particular advantages to commend it, in preference to others, for brass melting. Electric resistance furnaces have been used, but they again have not proved as suitable nor as attractive as other forms of electric melting. Arc furnaces of the rocking type find use, for the melting rate is high, control is easy and the carbon electrodes produce an atmosphere which is conducive to keeping down losses by oxidation. However, as already indicated, low-frequency induction furnaces are the most extensively used for production under continuous conditions.

So far as fuel is concerned, electric furnaces of whatever type have the advantage over solid- and liquid-fuel furnaces of cleanliness and greater flexibility of control, and, moreover, no arrangements are needed for either the handling or storage of fuel. Furthermore, the amount of manual work involved in the general manipulation and operation of such furnaces is usually less. With fuel-fired furnaces there is always the risk of contamination of the molten metal by impurities in the fuel such as, for example, sulphur in the form of gaseous compounds, and while brass may be less affected than many other alloys from this cause, the need for using fuel of suitable quality requires no emphasis.

Low-frequency induction furnaces, which over the last twenty years and more have proved their value both technically and economically as

melting units for continuous operation, range in capacity from about 600 to 2000 lb. of metal cast, some 300–2000 lb. of metal, depending on the size of the unit, being left in the furnace after pouring to maintain an adequate quantity of molten metal in the channel or ring, which constitutes in effect the secondary coil of a transformer, as well as a bath or reservoir for the incoming charge of solid metal. The time of the melting and casting cycle varies with the size of charge and number of ingots cast from each melt, but the period from the commencement of charging until the metal is ready for casting is about 50–55 min. The electrical consumption is about 265 kW. per ton of metal melted, inclusive of normal stand-by periods, but the net figure, related to melting only, is nearer 200 kW. The lining material for brass is a rammed alumino-silicate refractory, and the life, which is in a large measure determined by the composition of the alloy being melted, and, of course, by the treatment the lining receives, can be expected to run to some 4000 or 5000 tons. Much higher individual figures are not infrequently realized but, again, failures can occur after a comparatively small number of melts and are usually the result of faulty preparation and ramming. Once a furnace is put into operation, which it is by pouring an adequate quantity of molten metal into it to fill the channel after the rammed lining has been carefully dried and pre-heated, it is usually run so long as the lining remains intact. When not in active operation it is a common practice for the fully charged furnace to be put on stand-by load, that is, with a current input just sufficient to keep the metal molten, to avoid, not only the inconvenience and expense of recharging an emptied furnace, but, what is much more important, the very considerable risk of seriously damaging or ruining the lining. It is, however, possible to freeze the furnace, that is, to allow the residual charge to solidify *in situ* and then remelt when required. This is being practised to an increasing extent for economic reasons when the period involved exceeds about two days, but the procedures of cooling down and reheating both call for very special care and precautions.

IV.—Metal Melting.

The factors in metal melting of economic concern are to melt as speedily as possible with the minimum fuel consumption and metal loss, while those of technical or metallurgical interest are concerned with maintaining conditions of melting which will not lead to the quality of the metal being impaired. In short, to ensure that the metal suffers no contamination from contact with fuels, furnace gases, and products of combustion, from the refractory materials of the crucible

or furnace lining, or from stirring rods, rakes, &c.; that the molten charge is adequately mixed; and that it is raised to and poured at the appropriate casting temperature. With normal precautions all these factors can be adequately taken care of without serious difficulty in brass melting, although it will be quite clear, without any elaboration, that the different types of melting unit which have been already referred to vary considerably in the extent to which these hazards are present.

The risk of contamination from crucibles and furnace refractories is so slight as to be negligible, for usually these materials do not contain matter likely to be picked up and alloyed with the molten brass. In fact, the only likely contamination of the melt from this source is not chemical but mechanical in character, that is, from pieces of refractory material becoming detached and entangled with the molten metal, but such fragments float to the surface and are readily removed with the dross and any protective surface material which may be present. In many melting processes stirring rods and other similar appliances are not infrequently used, and if they are of iron or steel, as they nearly always are, there is a very considerable risk of an undesirable, and even serious, amount of iron pick-up, unless the working end is effectively covered, as it always should be, with a refractory wash or a closed-end refractory sleeve. The low-frequency induction furnace has the advantage over most other melting furnaces in that the molten charge is kept in a constant state of movement by thermal effects, which results in a very thorough and complete mixing without recourse to any stirring by manual means. Naturally, in all fuel-fired furnaces the risk exists, which is absent in electric furnaces, of contamination from contact with fuel and products of combustion, but this can be very largely avoided by good practice and the use of good-quality fuel.

In melting many non-ferrous metals the absorption of gas from the furnace atmosphere can exert a marked effect on the soundness of the casting. Hydrogen, for example, which is present in most furnace atmospheres, is a common cause of unsoundness in phosphor-bronze and aluminium castings. The solubility of gases in molten brass is, however, very low, because of the high vapour pressure of the molten zinc, and, therefore, degassing treatments do not form part of brass-melting procedures. Bailey [1] has suggested that the solution of chemically inert gas in brass decreases as the partial pressure of zinc approaches atmospheric pressure, just as the solubility of a gas in water decreases with increasing vapour pressure of the water, becoming zero at the boiling point. This theory was put forward to explain the soundness of brass cast from melts which had been treated with hydrogen, air, nitrogen, or sulphur dioxide, and Kroll, Anderson,

and Ball [2, 3] brought forward supporting evidence of the intrinsic freedom of liquid brass from dissolved gas. These latter workers employed a method of sampling by means of a scoop, which, after adequate pre-heating, was submerged in the molten brass and removed when filled to a pre-determined level. The molten alloy still in the scoop was rapidly quenched by immersion in mercury cooled with dry ice. Using the sample as a criterion of melt quality, it was shown that melt temperature and various gas treatments of liquid brass did not significantly affect the soundness or cleanliness of the metal, unless the sulphur content was raised to 0·14%, when inclusions were detected. Thus, in the casting of brasses containing substantial quantities of zinc, say, in excess of 15%, unsoundness due to high gas content in the melt is not significant.

Unless precautions are taken to avoid it, oxidation, with consequent loss of zinc, can take place to a considerable extent during the melting process. Usually with straight brasses the chief disadvantage arising from this is economic rather than metallurgical, that is, it is one of metal loss, for with anything like reasonably careful and understanding practices in dealing with the metal in the furnace, and its transference to the mould, oxide inclusions are not usually present in the casting. With brasses, however, to which certain alloying elements have been added, this matter of oxidation may not be quite so simple and calls for more attention. Zinc itself acts as a powerful deoxidant and, therefore, deoxidation does not normally feature in brass melting.

In liquid, and to a less extent in solid, brass, the high zinc vapour pressure results in a steady loss of zinc, and as long as an unprotected surface is exposed to the air, the zinc vapour diffuses outwards and eventually becomes oxidized, with the formation of a cloud of solid particles of zinc oxide. Because of the vapour evolution, there is little oxygen diffusion to the molten metal, and oxidation occurs at a distance from the metal surface. In practice the commonest method of protection in melting is the use of a charcoal cover which is maintained over the metal surface. This charcoal layer acts very largely as a barrier to the outward diffusion of zinc and the inward diffusion of oxygen, and these two reacting elements meet in the charcoal layer, forming zinc oxide which blocks the interstices in the mechanical barrier and so increases its effectiveness. Thus any disturbance of the cover results in an immediate evolution of zinc vapour from the exposed surface with the formation of a cloud of zinc oxide fume. Zinc loss is determined in some measure by the nature of the charge, such as the proportion and kind of scrap. Light and bulky scrap is awkward to charge and for ease of handling should preferably be baled. In the interest of

low loss by oxidation, solid metal should be charged through the protective layer into the molten metal beneath with the minimum disturbance, and solid metal should not, for any length of time, be exposed above the bath surface. Fluxes are quite often employed to supplement the barrier against zinc diffusion provided by the carbonaceous layer, and to facilitate, prior to pouring, the skimming operation, in which oxide, charcoal, flux, and any other foreign matter are simultaneously removed. Borax, boron compounds, glass, and mixtures of these substances are the most widely used fluxes in brass melting, and their action has been described by Thews.[4] One of the present authors [5] some years ago made an extended study of metal losses occurring in brass melting, and, in reporting on the losses resulting from varied operational conditions and protective and fluxing treatments, showed that the loss in low-frequency induction-furnace melting could be kept below 1% by covering the residual metal with a layer of charcoal before the commencement of charging, and when all the metal was melted, adding a mixture of borax and common salt which was stirred into the layer of charcoal and dross, all of which was skimmed off before pouring.

Many wrought brasses of both the alpha and more complex types contain specific additions of other elements such as lead, iron, aluminium, nickel, manganese, silicon, arsenic, and phosphorus, and their production may occasion appropriate modifications in melting procedure. Thus it is important to ensure that the added elements are effectively incorporated into the bath and that they do not suffer undue loss by volatilization or oxidation. In making complex or special brasses the constant movement and circulation of the molten metal without breaking or disturbing the surface from above as in stirring, which is realized in low-frequency furnace melting, is a very great advantage, particularly when adding elements such as aluminium and lead, the densities of which differ considerably from that of brass, or where any oxide formed is of a kind which may give rise to defects in the casting, as with aluminium and silicon. The effect of varying the method of adding lead in making free-turning brass has been studied by one of the present authors and Davis,[6] when it was shown that in melting in low-frequency furnaces the mixing was so complete and thorough that the lead distribution in the product was not sensibly influenced, either by the form in which it was added, or by adding it at different stages in the melting cycle. In making brasses containing iron the addition element is usually introduced as a ferro-zinc alloy, which should be added a sufficient length of time before pouring to ensure its complete alloying with the melt. Nickel, manganese, and silicon are usually added in the form of copper alloys, the lower melting points of which, as compared with those

of the elements themselves, facilitate alloying. Phosphorus is not commonly added to brass, but when it is, it is usually introduced as phosphor-copper, its effect on the alloy, in the molten state, being to decrease the viscosity to a very marked degree. Arsenic is added to some brasses in small quantity, that is, about 0·05%, to prevent dezincification of the product under certain service conditions, and is normally introduced as metallic arsenic towards the end of the melting operation. Aluminium is usually added in metallic form towards the end of the melting cycle and should be quickly and thoroughly mixed into the bath to prevent the formation of an aluminium-rich layer which is difficult to incorporate. In melting brasses containing such readily oxidizable elements as aluminium and silicon, particular precautions need to be taken to maintain conditions which will give rise to the minimum of oxidation, since oxides of these elements, if they enter the mould, are liable to cause defects in the casting.

V.—Moulds.

In the early days, ingot moulds for brass castings were of stone, but that was a long time ago and for much more than a century cast iron has been generally used as a mould material for brass ingots or slabs for rolling or billets for extrusion. Cast iron moulds are still extensively employed in the production of the multifarious shapes and sizes of castings encountered in the wrought brass industry. The advantages, however, of water-cooled, copper-faced moulds are so compelling that, although they are more elaborate and costly than solid iron moulds, they are always and unhesitatingly preferred in the production of ingots or billets in quantity for subsequent processing by modern methods on up-to-date plant.

The many limitations and disadvantages of cast iron which have been enumerated by Genders and Bailey [7] include low conductivity, which limits the chilling effect, progressive surface cracking, which adversely affects the surface quality and the soundness of the castings, and the reaction between the surface scale and carbon in the iron, which can give rise to blow-holes in the ingot surface. In spite of these shortcomings, however, the art of casting brass in iron moulds has been so perfected that brass castings of the highest quality are regularly produced.

Various types of iron have been used and critically studied as mould materials and the results of both experience and experiment indicate that of those so far available, a good-quality grey hæmatite iron is, in general, likely to give as good results as any. Usually, split moulds

are used for strip or ingot casting, the two halves being generally side- or bottom-hinged for vertical pouring, whereas the two halves of moulds used in the inclined position are completely detachable and are held together by rings and wedges. Apart from the larger ingots cast upright or vertically into water-cooled moulds, or flat-cast cakes or slabs for processing entirely by hot rolling, the sizes of so-called strip ingots for rolling, which are cast into iron moulds, generally range from about 3 to 16 in. in width, from about 1 to 2 in. in thickness, and from about 2 to 6 ft. in length. Billets for extrusion are cast both in iron and in copper-lined water-cooled moulds, but mainly in the former, which commonly range in diameter from about 3 to 8 in., with lengths ranging from 2 to 8 ft., although larger diameters are made for special purposes. These iron moulds are usually tapered and are known as solid or cannon moulds, although split moulds are used and have the advantage that the inside surfaces are more accessible for dressing and for cleaning after casting, which explains the superior billet surface obtained from such moulds.

In all types and sizes of cast iron mould, either solid or split, the volume of iron chill is usually rather more than double that of the ingot space. For the sizes of billets and ingots referred to, it is possible, with the appropriate conditions of pouring temperature, mould temperature, pouring speed, and so on, to achieve that measure of chilling which will ensure a solidification rate conducive to internal soundness and the formation of a crystal structure in the cast ingot which renders it suitable for subsequent mechanical processing operations.

Of those technical disadvantages of cast iron moulds which have been enumerated, the most significant is that due to progressive, and sometimes rapid, deterioration of the surface. Apart, of course, from shortening the useful life of the mould, it increases the difficulty of maintaining the production of castings of high quality. The mould deteriorates through the formation and development of lateral cracks which arise from the thermal shock the material sustains in pouring brasses at temperatures of over 1000° C. into a mould at about 100° C., and from the subsequent cooling of the moulds with water. Cracks usually begin to appear after only a very few ingots have been cast and become progressively deeper and more numerous, although their development can be delayed by careful treatment of the moulds which, after stripping, need to be cooled off by a uniform spraying with water over the upper portions.

The cracking of iron moulds can affect the quality of the casting in a variety of ways. The first fine cracks which form at an early stage in the mould life can be easily bridged and covered by the dressing and

because of their fineness hold no significant quantity of it. As the cracks develop and widen both dressing and cooling water easily penetrate and the latter may not always be completely dried out. This can give rise not only to blowing defects on the surface of the casting but also to increased porosity, actual measurements having shown that the porosity in brass ingots towards the end of the mould life is about twice that of ingots from new moulds. When the cracking of the mould surfaces becomes severe, the irregularities of contour are reproduced on the ingot surface with a corresponding deterioration in surface quality. These may be even so pronounced as to cause defects on rolling, and in extreme cases could interfere with the solidification contraction to such an extent as to cause hot tears on the ingot surface, but moulds in this advanced state of cracking are obviously quite unsuitable for use.

One of the outstanding advantages of the copper-faced water-cooled mould is that the copper surface, that is, the mould wall, does not crack in service like that of the iron mould, and, therefore, the surface condition of the ingot or billet does not progressively deteriorate with mould life, but, as regards the effect of the condition of the mould face, is as good on the last casting as it was on the first. The temperature of the water-cooled mould is lower than that of the iron mould and is automatically maintained within narrow limits, whereas the temperature of the latter is apt to be more variable since it is dependent entirely on circumstances and operators, a difference which contributes to the production of castings of more consistent quality from water-cooled moulds. When a cast iron mould has reached the end of its life it is entirely scrapped, whereas the copper-faced water-cooled mould usually requires only a replacement of the face plates.

Copper water-cooled moulds are constructed with relatively thin face-plates of wrought copper, the main framework, including the water-jacketing and piping arrangements, being of steel or cast iron. Slab moulds have rolled copper face-plates which are bolted or screwed into position, while billet moulds have solid-drawn tubular liners fixed into the outer casing with water-tight glands. A copper water-cooled mould necessitates a large supply of water during the period of casting, for the copper facing is normally only about $\frac{1}{2}$ in. thick and because of its high conductivity heat transfer is extremely rapid. Even with only the insulation of a thin mould dressing from liquid brass the copper face rises very little above the water temperature.

The life of water-cooled moulds is not, as already indicated, determined by surface cracking and deterioration, but by other causes such as bulging and failure at screw fixings and joints. Bulging of the copper face-plates of strip moulds is caused by differential expansion of the

inner and outer faces during the casting cycle. On 24-in. wide moulds the bulge is about 0·02 in. and is elastic in character, but with progressive use a permanent set is acquired and eventually the degree of bulging becomes unacceptable. Bulging also gives rise to stressing at the screw holes and may eventually lead to cracking at these locations, which is the other common cause of failure in moulds of this type.

VI.—Mould Dressings.

Mould dressings are a very significant item in the technology of brass casting, for according to how they are employed they can vitally affect the quality of the casting on these three critically important counts, internal soundness, crystal structure, and surface quality. The primary function of a mould dressing is to prevent contact between liquid metal and the mould surface, which might lead to adhesion or welding-on of the ingot, and to provide a uniform insulating film which controls the heat flow from the solidifying metal to the mould. Dressings fall into two distinct types, i.e. flaming and non-flaming dressings. Except in the case of special pouring and mould arrangements devised to promote quiescent or tranquil conditions, when non-flaming dressings are preferred, flaming dressings are generally used, for, in addition to successfully fulfilling the conditions already noted, they fill the mould with a reducing atmosphere almost as soon as pouring starts and help also in protecting the stream of molten metal from oxidation. Moreover, flaming dressings have an appreciable effect in refining the crystal structure of the casting which, other things being equal, is more marked with copper–zinc alloys of relatively high copper content such as gilding metals. This may be quite important in some circumstances, as for example in the casting of 67 : 33 brass for hot rolling.

Mould dressings are compounded from a variety of materials, and the inflammable constituent may be oil of various kinds, petroleum jelly, tallow, resin, &c., or a mixture of several of these, while the filler may be powdered charcoal, talc, china clay, &c. Non-flaming dressings usually consist of material such as bone ash or lamp black and may be applied dry or as an aqueous suspension with or without a wetting agent to improve the uniformity of spreading.

Dressings must be of such a consistency that they can be smoothly applied to the mould at the temperature normal for the particular type of mould. Thus, dressings containing resin are generally more suitable, and in consequence preferred, for iron moulds, whereas for water-cooled moulds which, as already mentioned, are operated at lower temperatures, oil-base dressings with powdered charcoal are more appropriate.

Careful preparation of dressings is important to ensure the elimination of any moisture and a thorough mixing of the constituents. Finely powdered charcoal is one of the most generally used fillers and it should be of such fineness that 95% passes a 240 British Standard mesh, for coarse particles of filler material can give rise to surface defects in the form of embedded dressing. The dressing must be of such a quality that when the volatile matter is burnt off it leaves an insulating film which is of sufficient strength to withstand the movement of the molten metal without cracking or breaking away, while after stripping out the ingot or billet it must be capable of easy removal.

The dressing should be so applied that it provides a smooth and uniform coating on the mould face, for excessive or irregular dressing is liable to give rise not only to surface defects but to sub-surface unsoundness. On the other hand, especially with relatively long moulds, a little additional dressing in the bottom of the mould is beneficial in avoiding defects on the surface at the lower end of the casting and in causing a rapid filling of the mould with reducing gas. Since iron moulds suffer from the progressive development of lateral surface cracks, they require greater care in dressing than copper-faced water-cooled moulds, for the useful life of the mould is affected by the protection provided by the coating, and as surface cracking becomes more severe, the skilful application of dressings can do much to minimize the deleterious effect of surface condition. In preventing the occurrence of defects of the type associated with mould surface condition, and more especially with the dressing, the importance of care in the preparation of the mould and in the application of the dressing can scarcely be overemphasized. After casting, the surface should be thoroughly cleaned by the complete removal of the residue of the spent dressing and of scale, and the mould carefully cooled down to a temperature suitable for the next application of dressing.

VII.—Pouring.

The transfer of metal from the melting unit to the mould is primarily a mechanical problem, and the first consideration is so to arrange conditions that the pouring stream is short, smooth, and unbroken, and that the carrying over into the mould of dross and other foreign matter is avoided. Vertical moulds are now generally used in brass casting and the metal is poured either directly from the melting unit or from a ladle into a tundish or runner box. The tundish should be kept full of liquid metal throughout the pouring period, so that it provides, in effect, many of the advantages of bottom pouring, and prevents any foreign material

which may have come over from the furnace or ladle from entering the mould, while it should also be accurately located with respect to the mould so that the stream or streams of molten brass do not impinge on the faces.

Inclined pouring, that is, pouring into moulds set at an angle to the vertical, has been largely superseded by vertical pouring, in comparison with which it has many disadvantages. The operation of pouring into such moulds is entirely manual and, therefore, the control of the stream, the rate of fill, and thus, in a considerable measure, the quality of the casting, depend on individual skill. It is not possible to fill the mould without the stream of molten metal impinging on the wall, which increases the liability to defects due to surface blowing, as well as decreasing the mould life as compared with that of vertical iron moulds. Moreover, it is much more difficult to prevent solid matter from coming over into the mould, and there is a greater risk of this, as well as of gas and dressing, being trapped.

In the casting of brasses containing aluminium the mechanical aspects of pouring are of special importance, for it is essential either completely to protect the liquid metal surface from the air, or, if it is exposed, to avoid turbulence, otherwise stable continuous aluminium oxide films are liable to be entrapped and cause surface defects or even internal discontinuities in the ingot. In Durville casting the metal is transferred to a container where it is allowed to remain undisturbed for a short time while it is carefully cleaned by skimming, and then, by rotating the mould and container, which are rigidly fixed together about a common axis, the metal is transferred smoothly into the mould without breaking the surface. The mould is almost invariably of cast iron and is preheated to about 100° C. Any dressings used are of the type free from volatile constituents so as to preserve the quiescent conditions, but in some circumstances dressings are entirely omitted. The surfaces of ingots successfully cast in this way are quite smooth and free from folds and cold shuts, but because a fairly high degree of super-heating is involved in the casting process and because of the small amount of turbulence, a coarse columnar structure in the ingot often results which may be undesirable for some purposes. The Durville process is more suited to the production of short ingots of relatively large section than long slender billets or slabs because of the difficulties associated with adequate feeding.

In the production of large castings, however, direct pouring by normal techniques, provided that these are carried out with care, might, in certain circumstances, be more appropriate than Durville pouring. Thus it is possible to produce large vertical castings of aluminium brass

consistently of satisfactory quality by direct pouring into copper-faced water-cooled moulds through a runner box. It is particularly important that the pouring stream be kept short and, as in Durville pouring, smooth and slow running, so that no significant breaking of the surface oxide film occurs. The metal flowing from the runner box into the mould is protected by gas evolved from the flaming dressing, except in the first few moments of pouring, when the splashing from the bottom of the mould may give rise to cold shuts and folds in the few inches near the base. Apart from this, ingots can be regularly produced not only with good surfaces but substantially free from harmful inclusions of aluminium oxide, and possessing a fine crystal structure associated with the use of a flaming dressing, which makes them very suitable for hot rolling.

The conditions necessary to ensure satisfactory feeding and the elimination of trapped gases in brass casting were established by Genders and Bailey,[7] and their conclusions, based on small ingots, have been found to be generally true over a wide range of ingot sizes. Mould chill, casting temperature and pouring speed are closely related factors which should be so adjusted with respect to each other that the solidification shrinkage in any given section of the casting can be adequately fed by hotter molten metal in the later stages of pouring.

The pouring speed is arranged to provide that rate of rise of metal in the mould which is associated with maximum smoothness and freedom from defects on the ingot surface. This is a factor additional to those enumerated by Genders and Bailey and appears to be governed by the rate of burning-off of the flaming dressing relative to the advance of liquid metal over the dressed surface. In brass casting the rate of filling the mould is about 1–1¼ in./sec. In actual practice the mould conditions are more or less fixed and also the rate of filling of the mould, and these, in consequence, define the optimum casting temperature for any given alloy within fairly narrow limits. The closeness of temperature control which is essential for the production of good quality products varies with circumstances. Ingots for hot rolling, for example, should generally be cast within $\pm$ 10° C. of the optimum temperature, although the latitude varies for different copper contents, as will be explained later. In casting smaller ingots into cast iron moulds, for cold rolling, a wider range may be permissible, since the crystal configuration is not generally of such importance in cold rolling. When using a furnace of the low-frequency type for melting charges of the same composition, the constancy of the energy input results in a time cycle for melting the charge and bringing it approximately to the correct pouring temperature, and with appropriate adjustments in time and input, which can

be made with some precision as a result of actual experience, and periodic pyrometric checking, reasonably constant pouring temperature can be maintained. When, however, ingots of 67 : 33 brass, for example, are being made for hot rolling, in which ingot structure is a factor of major importance, it is necessary to pour from accurately controlled temperatures.

Open-cast flat cakes for the production of large plates and the like are usually poured from ladles with wide pouring spouts, although direct pouring from the melting unit, such as a low-frequency furnace, is practicable, particularly when one mould can accommodate the whole charge. Pouring needs to be skilfully controlled to minimize the amount of splashing and to ensure a smooth flow over the mould bottom. In the subsequent filling of the mould the ladle should be oscillated slightly so that the impingement of the stream of molten metal is not localized and the possibility of the casting sticking to the mould bottom so reduced.

Feeding is a continuation of the process of pouring, and ingots and billets, whether cast vertically or inclined, must be adequately fed to eliminate as far as possible central unsoundness due to shrinkage cavities. Bridging should not be allowed to develop since it prevents further adequate feeding of the lower or remote portions of the contraction pipe. When several ingots are cast from one melt, the casting temperature needs to be so regulated that the feeding metal for the last ingot is not too cold to fulfil this function. Flat castings do not normally require feeding, since the pool of molten metal is shallow and contraction is, in the main, taken up by a more or less uniform lowering of the large surface area, although some interdendritic shrinkage cavities may also form in the surface layers. The upper surface of the ingot takes the form of a gentle curve, and the dip, for example, in the centre of a 4 ft. square casting 10 in. thick may be of the order of 2 in.

TABLE I.—*Casting Temperatures in ° C. for Brass Strip Ingots.*
(Super-heat is shown in brackets.)

Copper Content, %.	Chill Iron Moulds.	Water-Cooled Moulds.
80	1180° (175°)	1150° (145°)
70	1120° (168°)	1080° (128°)
67	1080° (147°)	1010° (77°)
63	1060° (147°)	1030° (117°)

The temperatures found by experience to be most suitable for brasses of copper contents ranging from 63 to 80% are shown in Table I, in which figures in brackets show the degree of super-heat above the liquidus temperature. When casting relatively small ingots for cold

rolling the super-heat required is of the order of 150°–170° C., while for larger ingots for hot rolling, cast into water-cooled moulds, it is only about 120°–140° C. A relatively low temperature is necessary in casting brass with 67% copper in a water-cooled mould in order to ensure a fine equi-axed grain structure in this alloy, which is difficult to hot roll without cracking if the crystal configuration in the casting is of the coarse columnar type. The straight copper–zinc alloys within the range of composition under consideration, under the conditions of casting already referred to, show very little segregation, but where conditions are such as to promote segregation during freezing, such as with a high degree of super-heat in a water-cooled mould, the segregation observed is invariably normal, that is, the outer portion of the ingot is higher in copper than the centre, although even under the worst conditions differences in copper content are small. Segregation of alloys is, in general, related to the freezing range, and Fig. 1, which is based on the latest data available,[8] shows the freezing range of copper–zinc alloys with up to 43% zinc content. The freezing range increases progressively with zinc content and under equilibrium conditions reaches a maximum at 67% copper. Thereafter it decreases sharply and the brasses with 55–63% copper for all practical purposes can be regarded as freezing at a constant temperature. In none of the brasses is the freezing range large in comparison with, for example, the copper–tin alloys, but nevertheless in the alpha range of alloys, that is, with 65–80% copper content, it can be sufficient to cause some segregation. On the other hand, in alloys containing from 55 to 63% copper, because of the small freezing range, segregation does not occur, and thus brasses of the alpha–beta type admit of a wider range of casting conditions. This applies also to the alloy containing 63% copper, which in the wrought condition is an alpha alloy. Thus, as might be expected, alloys with 63% copper content are relatively easy to obtain in a satisfactory uniform structural condition, and if suitable annealing conditions are observed in the later stages of rolling, a product free from the beta phase is readily obtained.

The 67 : 33 composition, on the other hand, corresponds to the maximum freezing range, and it seems not unlikely that hot-rolling difficulties with this alloy, except when poured under very carefully controlled conditions, are accentuated by segregation. Alloys with about 67–71% copper commonly show a small degree of normal segregation, which results in a somewhat low copper content in a narrow zone at the centre of the ingot. This occurrence was first described by Hull, Silliman, and Freeman,[9] and some further observations on the same phenomenon have been more recently reported.[10] It is most

readily revealed by shearing hot-rolled material, when a lamination at the centre is apparent, suggestive of central piping. In both ingots and hot-rolled products micro-examination reveals the presence of narrow bands of beta at the centre of the ingot, but in later stages of

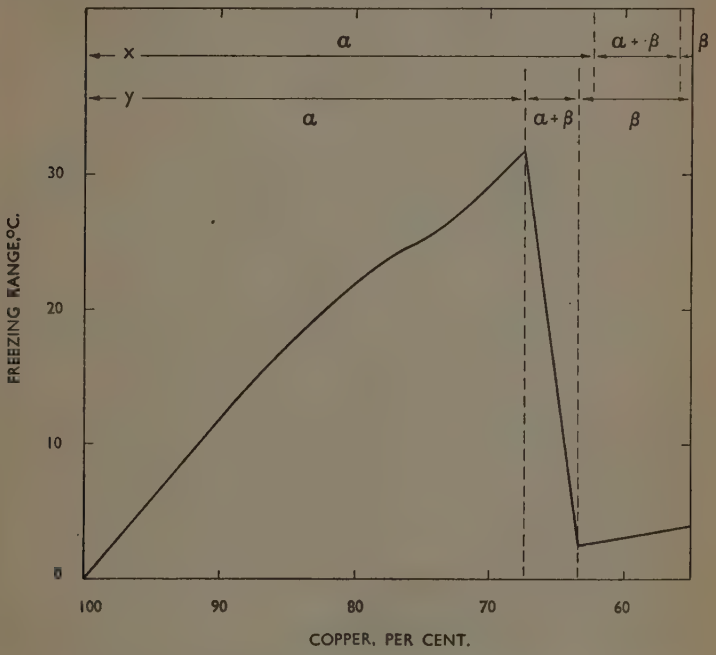

FIG. 1.—Freezing Range in Copper–Zinc Alloys under Equilibrium Conditions.
x Constitution: wrought alloys.
y Constitution at solidus.

fabrication the structure is converted entirely to the alpha condition by diffusion, although a narrow zone of somewhat finer grain-size may remain. These manifestations of segregation have been called phantom laminations, since they are apparent in the ingots but subsequently disappear. The earlier investigators [9] associated the phenomenon with interdendritic unsoundness as well as the presence of beta, but it seems probable that a slight degree of segregation is, in fact, the main phenomenon concerned.

Most of the ternary and more complex brasses normally show little or no segregation, which is, perhaps, not unexpected since the additions

generally have little effect on the freezing range, while dissolved gases, which are known to promote increased segregation, are, as already noted, not present to any appreciable extent in the brasses. One or two examples of inverse segregation have been reported, however; for example, Price and Phillips [11] have described exudations on the surface of Admiralty brass billets which showed 4% of tin on analysis, while the tin content of the body of the metal was 1·2%, but this is not normal experience. The presence of lead, of course, extends the freezing range, but under normal casting conditions the globules of lead are completely surrounded by solidified brass at an early stage and, therefore, any migration later in the freezing process cannot occur. In brass castings of the 60 : 40 type, lead contents of 3% and more can be readily obtained in a uniformly dispersed condition. In connection with the greater degree of segregation liable to occur in alloys with longer freezing ranges it is on record [11] that a brass containing 65% copper and 1% lead showed a lead content of as much as 2·8% on parts of the surface.

Although continuous casting is not within the scope of the present paper, processes of this type are being used to an increasing extent and have been for some years successfully employed in brass manufacture. Apart from economies resulting from continuous production and the absence of any end discard, as with discontinuously cast ingots or billets, and the facility of readily obtaining any desired length for subsequent fabrication, the process achieves progressive and controlled freezing or solidification and yields a high-quality product in respect of surface condition, internal soundness and crystal structure.

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THE MELTING AND CASTING OF NICKEL SILVER AT THE WORKS OF MESSRS. HENRY WIGGIN AND CO., LTD.* 1161

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Synopsis.

The equipment and technique developed by Messrs. Henry Wiggin and Co., Ltd., for the melting and casting of nickel silver of various qualities, are described. Oil- and coke-furnace crucible melting, and the special technique necessitated by the adoption of water-cooled moulds for casting strip ingots, are dealt with.

I.—Introduction.

The manufacture of nickel silver by Merry and Co., later known as Evans and Askin, nickel refiners and German-silver manufacturers, and later still as Henry Wiggin and Co., Ltd., was started in 1833. Since that date there have been many changes in technique and equipment, but this paper is concerned mainly with the melting practice at the Wiggin Street works of Henry Wiggin and Co., Ltd., as it developed from 1929 onwards.

During this period, nickel silver has been produced in qualities ranging from 7% to 30% nickel (typical compositions are shown in Table I), in the form of hot- and cold-rolled sheet and strip, extruded forms, and wire. These products are used in a variety of applications,

Table I.—*Approximate Compositions of Nickel Silver Alloys.*

Alloy.	Copper, %.	Nickel, %.	Zinc, %.
B.B.	53	30	17
A.1	55	25	20
Best	64	20	16
18%	63	18	19
Seconds	63	15	22
Thirds A	60	12	28
Fourths	60	10	30
Fifths A	62	7	31
Telephone Strip	55	18	27

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including spoons and forks, hollow-ware, telephone-contact springs, and decorative architectural work. As a base metal for silver plate, nickel silver is still the most popular of all alloys.

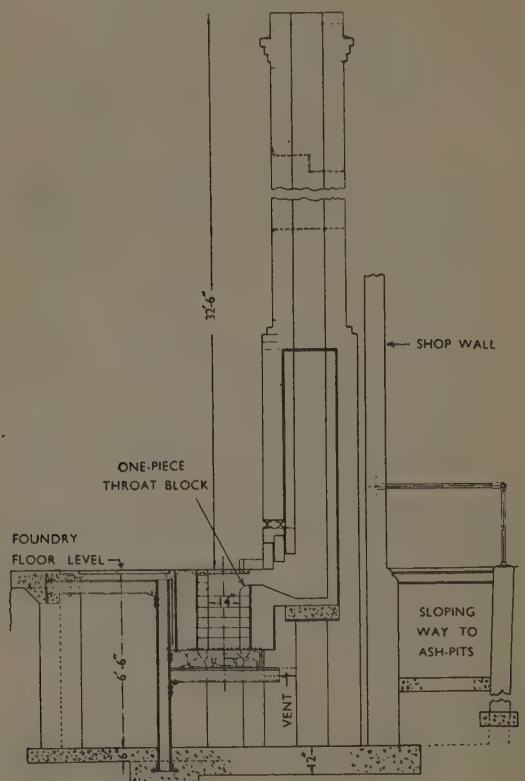

Fig. 1.—Design of the Coke Furnaces.

The melting procedures adopted for all nickel silvers are practically identical, the only variations being in casting temperature and ingot shape. Experience has been with the use of coke- and oil-fired furnaces only, and it is intended to deal first with the furnaces and ancillary equipment and then with melting practice.

II.—Melting Furnaces.

1. *Coke-Fired.*

These furnaces are of the natural-draught Wigley type, a drawing of which is reproduced as Fig. 1.

The design is particularly simple and trouble-free: maintenance consists largely of periodic relining with Stourbridge firebrick, after approximately 150 heats. Control of temperature depends on the skill of the caster in feeding his coke and keeping the "bed" clear and firebars clean, and in adjustment of the loose firebrick which is used in the flue as the main draught-control. Failure of the lining generally results from the gradual erosion of the lower half until a stage is reached when it becomes impossible to hold the coke in a bed round the crucible. A skilful caster knows just how far he may run a furnace lining without unnecessarily high coke consumption.

The best fuel for these furnaces is Durham hard coke, which, though costing 30% more than local coke, proves economical. Fuel consumption averages 0·57 lb. of coke per lb. of metal melted.

In all there are thirty furnaces, arranged in six shops of five furnaces each.

2. *Oil-Fired.*

In 1940 a battery of twelve nominal-200 lb.-capacity, lift-out-type oil-fired furnaces was installed, in a specially built melting shop. The design of the furnaces is shown in Fig. 3 (Plate XXXVIII). A furnace can quickly be replaced by simply disconnecting the oil- and air-supplies and lifting it out of the pit. The decision to install small lift-out furnaces, instead of larger tilting-type furnaces with rotary mould beds, was based primarily on the opinion that better control of pouring conditions can be obtained when casting a small quantity of metal manually into small moulds.

The original furnaces were lined with shaped alumina firebricks and were fitted with removable bottoms. Using this construction, the life averaged 300 heats, and the cost of relining, in 1940, was £20 per furnace. Subsequently, the lining was changed to a rammed silicon-carbide mixture, backed with insulating bricks and formed round a greased iron cylinder which could be easily removed. A burner block of silicon carbide is used, and fettling of the furnace walls is carried out using a silicon-carbide slurry applied with a brush.

The furnace bottoms have also been modified so that they are formed by a 4-in. layer of loose sand rammed on two steel flaps which can be conveniently dropped when a new bottom is required, a central plumbago block being provided for mounting the crucible.

If the crucible should fail in the furnace, a thin metal diaphragm, covering a hole in the bottom plates, can be easily pierced, allowing the metal and slag to fall into the space below the furnace, where they will do no harm. The furnace bottoms require replacing about

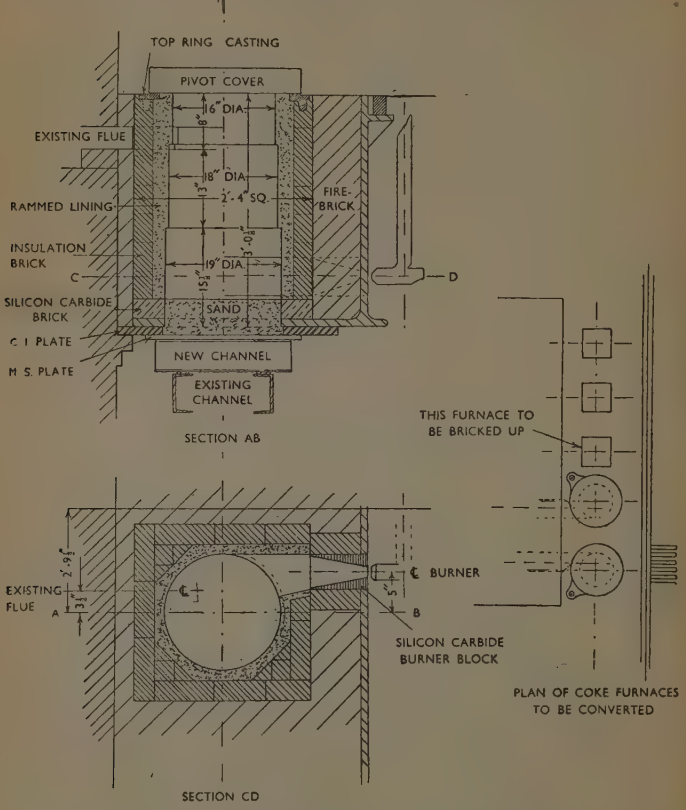

FIG. 2.—Conversion of the Coke-Fired Furnace to an Oil-Fired Furnace.

once every 50 heats, the principal reason for replacement being the accumulation of slag and metallics at the bottom of the furnace. These changes in the furnace construction have increased the life to over 3000 heats. The relining cost, in 1941, for this type of lining,

was £50, and the resulting decrease in operation cost per pound of metal produced is obvious, though the greatest advantage arises from the ability to run the furnaces for long periods without shut-down and with only a small amount of attention.

Owing to war-time restrictions, the fuel originally used was creosote pitch, and, after the change of linings referred to above, the principal maintenance charge was the regular and frequent cleaning of the burners necessitated by the use of this fuel. However, a technique was developed to overcome the stoppages due to the lack of fluidity of the fuel and to the choking of the burners by solid particles. Each group of burners was fed from a small gravity tank immediately above the furnaces. These tanks were electrically heated, their temperature being thermostatically controlled, and the pitch was led to them through electrically heated pipe-lines. The level of pitch in the tanks was controlled by ball valves. By this means, differences in temperature and fluidity in the long main line were rendered innocuous, larger burner orifices were possible, and stoppages ceased. Once this difficulty had been overcome, the creosote-pitch installation became a most efficient fuel arrangement; but recently fuel oil became more generally available and was substituted for creosote pitch, thus rendering unnecessary the precautions to keep the fuel fluid. Oil consumption averages 0·3 lb. per lb. of metal melted.

In 1942, two of the furnaces in one of the coke-fired-furnace shops were converted for oil-firing, as shown in Fig. 2. These proved most successful, and a shop fitted with two oil-fired and two coke-fired furnaces produces as much metal as a shop fitted with five coke-fired furnaces. Photographs of this shop, in operation, are shown in Figs. 6–10 (Plates XL and XLI).

III.—Crucibles.

During recent years, it has been the general practice to use the silicon-carbide type of crucible. Before the introduction of this type of crucible, graphite crucibles had been used. The reason for the change arises from the higher thermal conductivity of the graphite, which, though being an advantage during the melting of the metal, in that it reduces the melting time, proved a disadvantage when the casting into water-cooled moulds of more than one ingot from one heat of metal was commenced. The greater thermal conductivity of graphite resulted in a greater rate of cooling, particularly when the crucible walls were becoming thin, and it was found that if the first ingot was cast at the correct temperature the later ingots showed porosity, due to too low a

pouring temperature, and that if the casting temperature of the first ingot was raised so that the second ingot was sound, a defective first ingot resulted, and the mould life was considerably reduced. The lower thermal conductivity of the silicon carbide overcame this difficulty, though the melting time was slightly increased.

The life of the graphite crucible in coke-fired furnaces was of the order of 25–30 heats, and that of silicon-carbide crucibles was of the order of 40–50 heats. In the oil-fired furnaces it is possible to obtain lives of from 60 to 80 heats per crucible, largely because of the absence of the abrasive action of the coke and furnace tools on the outside of the crucible. The rejection of a crucible has always been the responsibility of the caster, as an experienced man can judge when the crucible has been so weakened that there is a risk of the breaking of the crucible full of molten metal, leading to serious burns. In addition, the thinner the walls of a crucible the greater the danger of the pick-up of gas by the metal from the furnace atmosphere through the crucible wall.

The life of crucibles has been effectively extended by a careful arrangement of the melting schedule, by which crucibles are first used for the melting of high-grade high-nickel-content alloys and, as their condition deteriorates, for lower-grade low-nickel-content alloys.

In the early days, crucible consumption was high, but after the introduction of a " pot bonus " crucible lives were greatly increased. This bonus allowed the caster 25% of the sum saved when the life of the crucibles exceeded a standard life figure, this figure being agreed by the casters for different types of crucible and furnace.

The majority of the crucibles fail owing to thinning of the walls, resulting from the burning of the outside by the flame, erosion of the outside by the coke, and internal erosion at the flux line. This latter cause was initially very serious when a mixture of borax and boracic acid was used as a flux. Later, the melting flux was changed to " Boro-calcite " and this erosion became much less severe.

IV.—Moulds.

Initially, the standard type of split cast iron mould was used for all types of nickel silver ingots. Split moulds were adopted because of the ease with which they can be examined and dressed, as compared with the solid type, and it was usual to specify best hæmatite for their manufacture. Failure is generally due to surface deterioration and to warping at the joints. No repair of moulds is carried out except in the case of the 4-in. wire-bar moulds (see Table II), where the moulds

are occasionally shortened by removing a length at the bottom of the mould, a position at which erosion by the metal stream is severe.

TABLE II.

Type of Ingot.	Size of Ingot, in.	Weight of Ingot, lb.	Type of Mould.
Strip	$18\frac{1}{2} \times 5\frac{5}{8} \times 1\frac{1}{2}$	50	Water cooled.
,,	$20\frac{1}{4} \times 6\frac{5}{8} \times 1\frac{15}{16}$	80	,,
,,	$23 \times 7\frac{1}{4} \times 2\frac{1}{16}$	100	,,
,,	$32 \times 8 \times 2$	155	,,
,,	$29 \times 10 \times 1\frac{7}{8}$	160	,,
Wire bar	$28 \times 4 \times 4$	136	Cast iron.
,,	32×4 in. dia.	136	,,
Extrusion billet	$9 \times 7\frac{1}{2}$ in. dia.	170	,,

The life of cast iron moulds depends largely on the quality of metal being cast. The higher the nickel content the shorter the mould life, as a result of the higher pouring temperature, an average life of a 50-lb. mould being approximately 100 strips. The cost of a 50-lb. strip mould in 1936 was 25*s.* and in 1947 £3.

In 1922 Wiggin co-operated with Junker in the use of water-cooled moulds, and several 80-lb. units were installed at Wiggin Street. Later, water-cooled moulds of other sizes were introduced, and finally all strip ingots were cast in these moulds, though the technique has never been applied to any other type of ingot. The main body of each mould is in cast iron, and the copper plates which form the mould itself are machined from the solid. This method of construction ensures that no joints occur at the long corners of the mould, thus avoiding sticking by penetration of metal in the corners. The main copper plates are replaced annually, the only other maintenance required being the replacement of the copper strip forming the bottom of the mould when it is eroded by the impact of the metal stream, and the renewal of the glands in the hinges of the mould, which also carry the water supply to the front section.

The earlier moulds had radiused corners, but it was later found that these radii on the ingots greatly increased the likelihood of edge-cracking during rolling, and later moulds were made with square corners, which eliminated the trouble.

The types and dimensions of the moulds at present in use are shown in Table II. The ratios of the dimensions which give a satisfactory ingot for a given weight and type of billet have been developed gradually. The majority of the metal for cold rolling to strip and sheet is cast in 50-lb. ingots, as this was found to be the ideal size for man-handling,

rolling, and annealing, using the equipment available, and the most suitable size for many of the orders received. The larger strip ingots are hot rolled. All the strips cast are rectangular in shape and are not " bellied ", for it is the practice for all ingots to be machined before rolling.

It will be noticed that a one-piece cast iron mould has been introduced for the casting of extrusion billets. It was found that this type of mould, used with a very large feeding head, gave the most satisfactory results for this type of ingot.

The cost of a 50-lb. water-cooled mould in 1936 was about £65 and in 1947 £200–240. Renewal of the copper plates, including the purchase of the material, cost £30 in 1936 and about £100 in 1947.

V.—Shop Arrangement and Other Equipment.

1. *Coke-Fired Furnace Shops.*

The arrangement of a coke-fired melting shop may be seen in Figs. 1 and 7–10 (Plates XL and XLI). The arrangements for casting into a water-cooled 80-lb. mould, and the casting pit for the cast iron moulds, can be seen. The use of a support for the tail of the shank, which enables the caster to control the crucible himself, is simple, and can readily be adopted in any existing melting shop where it is desired to obtain vertical pouring through tundishes. Of the coke-furnace shops, one is fitted with an 80-lb. water-cooled mould, two are fitted with two 50-lb. water-cooled moulds, and three are fitted with racks for cast iron moulds for wire bars and extrusion billets. In the shop illustrated, a hand-operated hoist-block has been installed, to facilitate the lifting of the crucible from the furnace and the handling of the moulds.

2. *Oil-Fired Furnace Shop.*

The lay-out of the oil-fired melting shop is shown in Figs. 3 and 4 (Plates XXXVIII and XXXIX). The designs show the arrangement for casting into cast iron moulds, but the casting pits are so arranged that either water-cooled moulds of various sizes or cast iron moulds of different types can be installed. Pouring in this shop is carried out using a trolley which holds the crucible. The crucible is removed from the furnace and placed in the trolley, using a 5-cwt. hoist-block. A drawing of the trolley is reproduced as Fig. 5, by courtesy of the designers, the Aston Chain and Hook Co., Ltd.

An overhead power crane is available for lifting the cast iron moulds from the bed, for stripping and replacement in the beds, and for handling the completed ingots.

THE ELASTIC PROPERTIES OF METALLIC ALLOYS.* 1162

By R. CABARAT,† Professor L. GUILLET,‡ and R. Le ROUX.§

(Translated by H. W. L. Phillips, M.A., Member.)

Synopsis.

The object of this investigation was to study the effect of constitution on the elastic modulus and logarithmic decrement in copper–tin and copper–zinc alloys. The method employed consisted in setting up by electrostatic means longitudinal vibrations in the specimens, thereby submitting them to very small strains at a high frequency, all measurements being made in free air. In the two systems, the δ and γ phases, which have multi-atomic cells, are shown to have high moduli of elasticity with low values for the internal friction, whereas the curve showing the relationship between the latter property and the composition shows maxima for the phases β (body-centred cubic) and ϵ (hexagonal). Changes of the decrement with composition follow closely those of the electrical conductivity. The experimental data are discussed in the light of current theory.

I.—Introduction.

Measurements of physical properties have often been used to obtain confirmation of the constitution of alloy systems as determined by thermal analysis or crystallographic methods. Little use has, however, been made of the elastic properties in this connection. In the case of brittle alloys, experimental difficulties are very great, and the majority of investigators have limited their work to a study of the changes occurring in solid solutions. For example, Chevenard and Portevin [1] showed that, at constant temperature, the modulus of elasticity varied linearly with the chemical composition, while the internal friction, as estimated by the logarithmic decrement of the decay of the amplitude of the vibration, varied in a manner similar to that shown by the electrical conductivity. In 1936, one of the authors,[2] using a dynamic method due to Le Rolland and Sorin,[3] showed that exceptionally high values of the elastic modulus were reached in the case of certain intermetallic compounds of which the structure had been established, and these results were later confirmed by the work of Köster [4] and by that of Druyvesteyn and Meyering.[5] Very recently, in 1946, the present

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authors succeeded in demonstrating by means of the micro-torsion testing machine introduced by Chevenard,[6] and later perfected by Boulanger,[6] that the internal friction shown by these particular compounds was extremely low.[7]

It appears to be generally agreed that for work of this kind, dynamic methods imposing only very small strains at high frequency possess undoubted advantages : they obviate the occurrence of those transient or permanent changes associated with mechanical deformation which give rise to the well known phenomena of elastic after-effect and work-hardening. This is the reason for the increasing use now being made of electro-magnetic methods, as for instance in the investigations of Zener and Randall,[8] Read,[9] Förster,[10] and Frommer and Murray.[11]

Some years ago, one of the authors, working in the Testing Laboratory of the Conservatoire National des Arts et Métiers, developed a new apparatus for determining the elastic properties, complying fully with these requirements, in which the test-piece was submitted to longitudinal vibrations produced electrostatically.[12] The chief object of the present investigation was to show that this apparatus could be used in correlating changes in the elastic properties with constitution. The alloys of copper with tin and of copper with zinc were chosen for study because their constitution is now sufficiently well established.

II.—Experimental Methods.

The dynamic method used is based on the classic relation between the velocity of propagation, V, of a longitudinal wave in a specimen of modulus of elasticity E and density d. For test-pieces of the dimensions used a simple formula can be employed :

$$V = \sqrt{\frac{E}{d}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which E is Young's modulus. For specimens in which the cross-section is not negligible in comparison with the length, a formula due to Lord Rayleigh [13] should be used :

$$V = \sqrt{\frac{E}{d(1+e)^2}}$$

in which

$$e = \left(\frac{\pi\sigma z r}{2L}\right)^2$$

where σ = Poisson's ratio, z = number of half wave-lengths in the whole rod, r = radius of rod, L = length of rod. Taking a value of 0·37 for Poisson's ratio, it can be shown that for test-pieces of dimen-

sions used in this research $(1 + e)^2 = 1{\cdot}0086$ approximately. Thus the error introduced by neglecting the Rayleigh correction is extremely small. Boyle and Sproule [14] have shown that an additional correction may be needed to cover the effect of coupling between the longitudinal waves in the rod and the transverse waves which they engender. The correction, however, is negligible if $\frac{zr}{L}$ does not exceed 0·55, a condition which is met in the case of rods of the dimensions given vibrating in the fundamental mode. Stokes [15] has shown that the velocity of propagation is lowered by internal friction, the formula being :

$$V = \sqrt{\frac{E}{d} - \left[\frac{4}{3}(1 + \sigma)\frac{n}{d}\frac{\pi}{\lambda}\right]^2}$$

where n is the coefficient of internal friction. Here again, for the frequency used, the correction is negligible. Röhrich [16] has taken thermal conductivity into account, and has shown that an adiabatic modulus E' should be used in the formulæ, related to E by the expression :

$$\frac{E}{E'} = 1 - \frac{\alpha^2 TE}{dc}$$

where α = linear coefficient of expansion, T = absolute temperature, and c = specific heat at constant pressure. The correction is again very small.

If the test-piece, of length L, is vibrating at a frequency F_0, with a node at the middle, the wave-length λ is given by the expression :

$$\lambda = 2L = \frac{V}{F_0}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Combining equations (1) and (2) :

$$E = (2F_0L)^2 d \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In the apparatus shown diagrammatically in Fig. 1, a cylindrical test-piece 140 mm. long and 8–12 mm. in dia. is held vertically between two adjustable electrodes A and B by means of three hardened steel needles at the node, i.e. the mid-point of its length. The diameter of the test-piece need not be exactly specified, but must be uniform. The two electrodes A and B form, with the flat ends of the test-piece, the plates of an electric condenser. The electrode A is coupled, through an amplifier, to the output of a low-frequency heterodyne oscillator, and exerts a periodic electrostatic attraction on the test-piece, thereby setting up in it longitudinal vibrations. The electrode B functions as an electrostatic microphone. Potential variations set up in it by the vibration of the test-piece are amplified and applied to a cathode-ray

oscillograph, and may be measured by means of a thermionic voltmeter. The test-piece itself must be at earth potential.

The vibrations in the specimen only become appreciable when the frequency of the applied voltage is equal to the frequency of free vibration of the specimen. The variable condenser of the oscillator is therefore rotated until resonance is obtained. At this point the amplitude of the vibrations reaches a sharp maximum, and the corresponding

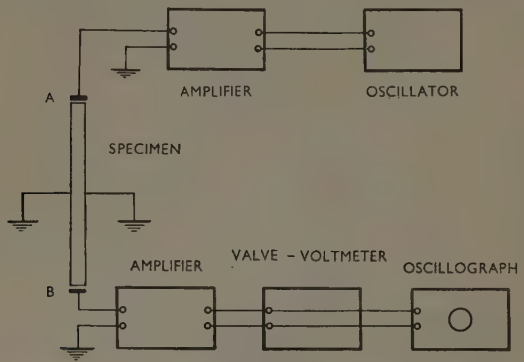

FIG. 1.—Diagram of the Apparatus Used for Measuring the Elastic Modulus and Internal Friction.

frequency F_0 is read off from the dial of the condenser, which has previously been calibrated. The value of the modulus is then determined by means of equation (3). The frequency, which is checked by comparison with a standard provided by the Laboratoire National de Radioélectricité, can be read to ± 5 cycles per second, involving a relative error of 5×10^{-4}. The length can be measured to $\pm$ 10 microns, involving a relative error of 6×10^{-5}, while the error involved in determining the density is 1 to $2{\cdot}5 \times 10^{-3}$. The values calculated for the modulus are therefore subject to an error of the order of 0·36%. Successive determinations of the modulus made on the same specimens have, in fact, given results differing by less than 0·4%.

The logarithmic decrement of the decay of the amplitude of successive vibrations is usually taken as a measure of the internal friction of the material. Its value is given by the expression :

$$\delta_0^n = \log_e \frac{A_0}{A_1} = \frac{1}{n} \log_e \frac{A_0}{A_n}$$

where A_0 = initial amplitude, A_1 = amplitude after one complete

oscillation, A_n = amplitude after n complete oscillations, and e = base of natural logarithms.

In practice, δ may be calculated from observations of the time for the amplitude A_n to fall to a definite fraction of A_m, but it may also be determined from the breadth of the resonance curve when the specimen is in forced vibration (Fig. 2), and this method has been used in the present investigation. It is easy to show that if ΔF is the breadth of the resonance curve at an amplitude of $\frac{A_m}{\sqrt{2}}$ then :

$$\delta = \pi \frac{\Delta F}{F_0}$$

where F_0 is the resonance frequency. The error of the determination is rather higher than that given above for the modulus, and it is probable that it is of the order of 5%.

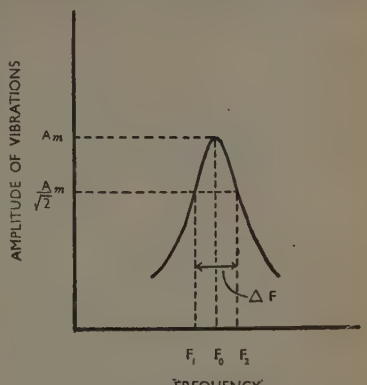

Fig. 2.—Resonance Curve.

Fig. 3 (Plate XLII) gives a general view of the apparatus. It should be mentioned that all measurements were made in free air.

III.—Elastic Constants of Pure Metals.

The value of the decrement for pure copper given in Tables III and IV, namely $79{\cdot}4 \times 10^{-4}$, is higher than that usually quoted in the literature. The authors have found, however, that the decrement is appreciably affected by the oxygen content of the metal, as the values given in Table I show.

Table I.—*Properties of Copper.*

Oxygen, %.	Log. decrement, δ, $\times 10^4$.	Specific Resistance, ohms/cm.^{3}/cm., at 20° C.	Temp. Coeff. of Resistivity, $\frac{1}{\rho} \times \frac{d\rho}{d\theta} \times 10^3$.
0·017	79·4	1·695	399
0·024	78·3	1·695	400
0·044	54·6	1·695	399

It will be seen that the decrement decreases with increasing oxygen content, whereas the electrical resistivity and the temperature coeffi-

cient of resistivity (the latter measured over the range 20°–57° C.) remain constant. The test-pieces used for these experiments had been annealed for 15 hr. at 600° C. and had a grain-size of 300 grains/mm.^{2}

In the case of tin, the decrement also falls with increasing content of impurities, as shown by the figures quoted in Table II.

The values for the modulus and decrement given in Table IV for zinc, 8·935 kg./mm.^{2} and $7{\cdot}60 \times 10^{-4}$, respectively, were measured on chill-cast annealed specimens. Very scattered values are obtained on rolled or drawn specimens because of the markedly preferred orientation

TABLE II.—*Properties of Tin.*

Antimony, %.	Lead, %.	Iron, %.	Arsenic, %.	Copper, Silver.	Log. decrement, $\delta \times 10^4$.
0·04	0·03	0·01	trace	traces	75
0·19	0·07	0·06	0·005	traces	51·2

and elastic anisotropy of such material. Values measured on a single crystal, produced by recrystallization, of which the glide planes were inclined at an angle of 32° to the axis of the specimen, were 12·039 kg./mm.^{2} for the modulus and $3{\cdot}5 \times 10^{-4}$ for the logarithmic decrement.

IV.—Elastic Constants of Copper–Tin Alloys.

Except for alloys containing less than 10% tin, which could be rolled, the alloys were chill cast. Cast α bronzes are somewhat unsound, because of their long solidification interval and high gas content, so that values of the elastic constants determined on such materials are subject to considerable scatter, particularly so in the case of the logarithmic decrement. In general the alloys were annealed for 100 hr. at the maximum temperature compatible with the equilibrium diagram, and were then cooled at an average rate of 1° C./min. An exception was made in the case of alloys containing 30–50% tin : here, because of the slowness of diffusion, an annealing time of 1000 hr. was adopted. All specimens were examined for soundness by radiographic means, and by comparing the experimentally determined value d_e of the density with the value d_c calculated from lattice-parameter measurements. The values are given in Table III, and the modulus and decrement are shown plotted against atomic percentage of tin in Figs. 4 and 5.

It is generally accepted that in the copper–tin system there are three intermediate solid-solution ranges, designated δ, ε, and η', as indicated in Figs. 4 and 5. Only the first of these phases corresponds with a stationary point, a maximum, on the modulus–composition curve, but

all three correspond with stationary points on the decrement–composition curve, δ and η' with minima and ε with a maximum. It is interesting to note that the shape of the decrement–composition curve is very similar to that of the electrical conductivity–composition curve.[17]

TABLE III.—*Elastic Properties of Copper–Tin Alloys.*

Tin, at.-%.	Density.		Length, L, mm.	Frequency, F_0, c./s.	Modulus, E, kg./mm.^{2}	Breadth of Resonance Curve,* ΔF, c./s.	Log. decrement, δ, $\times 10^4$.
	Measured d_0.	Calculated d_c.					
0	9·058	9·02	139·94	13,262	12,730	33·5	79·4
1·8	9·040	9·02	139·72	13,460	13,036	6·5	15·4
2·6	8·990	9·02	140·10	13,140	12,423	1·3	3·11
3·2	8·984	9·02	140·14	13,040	12,216	2·3	5·54
5·6	9·128	9·03	139·93	12,887	12,102	1·8	4·36
15·1	9·040	...	132·22	13,640	11,989	2·5	5·76
20·0	9·084	9·05	129·57	15,001	13,993	1·45	3·04
22·6	9·096	...	135·78	14,005	13,412	4·4	9·87
24·5	9·120	9·10	138·94	12,157	10,609	9·2	23·8
31·6	8·852	...	133·50	12,698	10,368	3·05	7·55
34·9	8·519	...	136·10	12,630	10,264	2·05	5·1
40·0	8·452	...	132·90	12,969	10,238	2·85	6·91
41·8	8·370	...	138·00	11,903	9,207	3·3	8·70
44·5	8·400	8·20	134·48	12,453	9,606	6·5	16·4
68·1	7·837	...	135·92	10,814	6,904	10·3	29·9
100·0	7·320	7·35	137·54	9,847	5,475	23·5	75

* Corresponding to an amplitude $\frac{A_{max.}}{\sqrt{2}}$

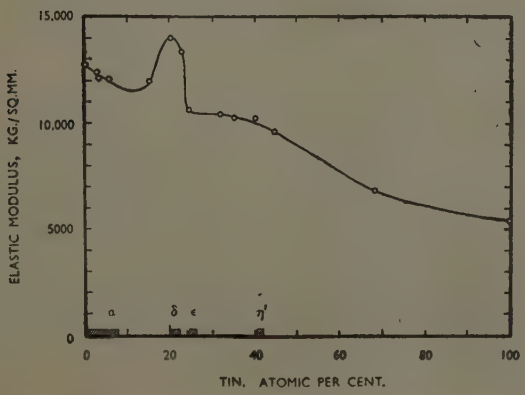

FIG. 4.—Variation of Elastic Modulus with Chemical Composition: Copper–Tin Alloys.

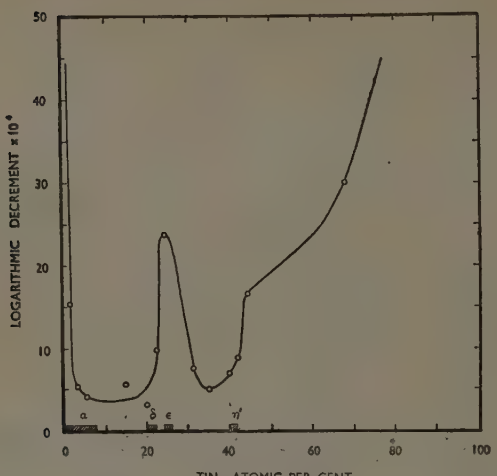

FIG. 5.—Variation of Decrement with Chemical Composition: Copper–Tin Alloys.

V.—ELASTIC CONSTANTS OF COPPER–ZINC ALLOYS.

Alloys were prepared from electrolytic copper and zinc. From 0 to 35% of zinc, test specimens were prepared from rolled bars, but with higher percentages of zinc, sand castings were made, the Durville process being used to ensure maximum soundness. The specimens were annealed and checked for soundness in the manner described for the copper–tin alloys, and were machined to size, except in the case of the alloys consisting of the γ phase, which were ground by hand. The results obtained are given in Table IV and have been plotted in Figs. 6 and 7.

These alloys are very suitable ones to study from the point of view of the present research, because of the marked changes in structure associated with changes in composition. There are three intermediate phases, β, γ, and ε, having respectively body-centred cubic, multiatomic cubic, and hexagonal cells. The β phase, which has pronounced metallic characteristics, is associated with a maximum on the decrement–composition curve lying at a zinc content somewhat below that corresponding to the intermetallic compound CuZn. Microscopical examination showed, in fact, that alloys containing more than 48·8 at.-% zinc contained some γ phase. Although alloys consisting of the β phase can be rolled at high temperatures (700° C.), it was thought advisable

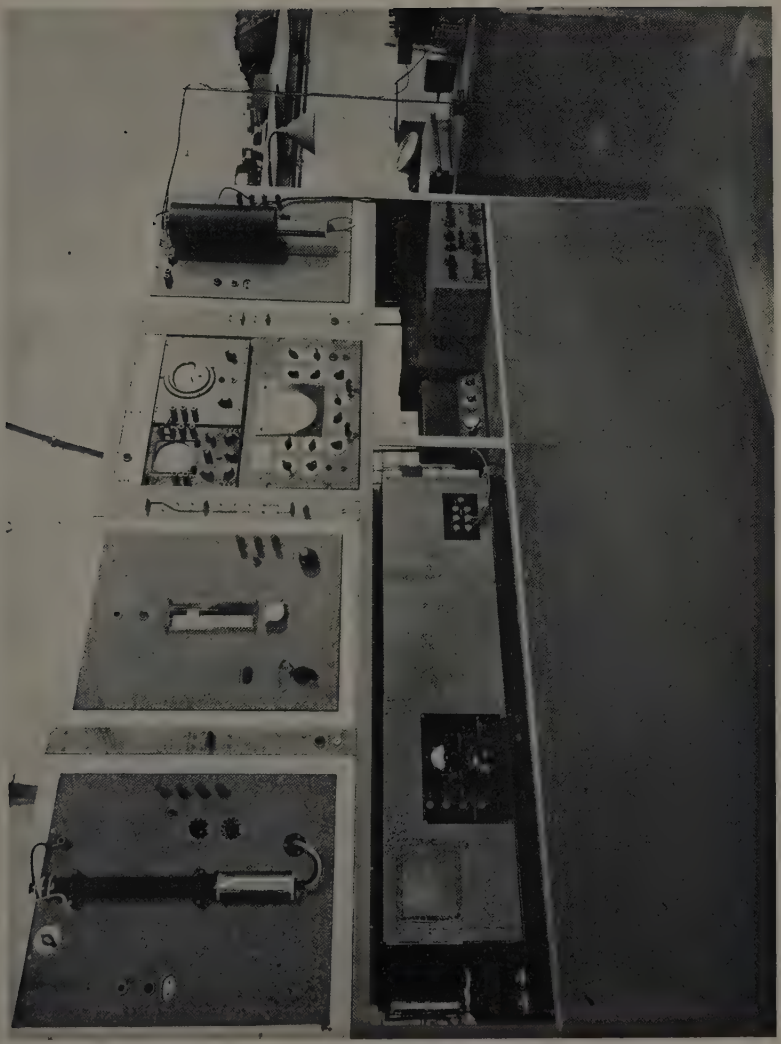

Fig. 1. General View of Apparatus.

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to use cast test-pieces : this phase possesses marked elastic anisotropy,[18] and the presence of even small amounts of preferred orientation leads to low values being obtained for the elastic modulus, and pronounced scatter in the values for the decrement. For these alloys, to ensure a

TABLE IV.—*Elastic Properties of Copper–Zinc Alloys.*

Zinc, at.-%.	Density.		Length, L, mm.	Frequency, F_0, c./s.	Modulus, E, kg./mm.^{2}	Breadth of Resonance Curve,* ΔF, c./s.	Log. decrement, δ, $\times 10^4$.
	Measured d_e.	Calculated d_c.					
0	9·058	9·02	139·94	13,262	12,730	33·5	79·4
4·4	8·913	8·95	139·92	13,460	12,890	4·3	10·1
9·8	9·116	8·85	139·55	13,246	12,665	2·15	5·1
29·7	8·555	8·60	139·60	13,025	11,533	1·75	4·22
34·4	8·565	8·50	139·50	12,760	11,065	1·85	4·55
48·0	8·308	8·35	139·80	12,270	9,968	2·95	7·1
55·1	8·173	...	139·84	14,040	12,846	1·25	2·8
59·9	8·073	8·10	149·90	14,425	15,391	0·76	1·68
61·3	8·063	8·08	149·90	14,427	15,376	0·85	1·88
66·6	7·913	7·95	149·00	14,690	15,457	2·05	4·38
73·0	7·745	...	156·90	13,155	13,453	2·50	5·97
80·2	7·480	7·72	149·22	13,250	11,923	2·00	4·75
92·9	7·495	...	139·77	13,795	11,361	1·85	4·22
100·0	7·266	7·22	139·88	12,415	8,935	3·0	7·60

* Corresponding to an amplitude $\frac{A_{max.}}{\sqrt{2}}$

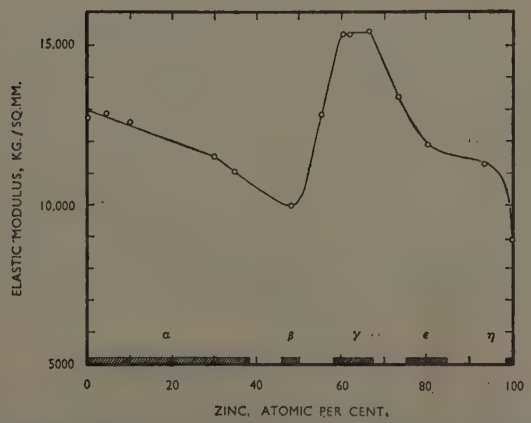

FIG. 6.—Variation of Elastic Modulus with Chemical Composition: Copper–Zinc Alloys.

fine grain-size (600/cm.^{2}), an addition of 0·25% titanium was made to the melt, and a graphite mould was used. It is interesting to compare the experimental value of the modulus for the β phase (9968 kg./mm.^{2}) with that calculated, for an aggregate of crystals oriented at random, by means of Bruggeman's formula.[19] From data derived from mea-

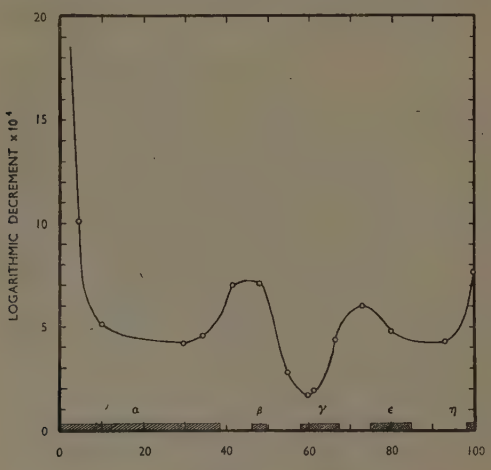

FIG. 7.—Variation of Decrement with Chemical Composition: Copper–Zinc Alloys.

surements on a single crystal, the calculated value for an aggregate lies between 10,000 and 11,530 kg./mm.^{2}, which is only slightly higher than the value found experimentally.

The phase ε, like β, corresponds with a maximum on the decrement curve, while γ, of which the metallic characteristics are less marked, corresponds with a minimum. The latter phase is associated with an absolute maximum on the modulus–composition curve.

These results are in exact conformity with those obtained in the copper–tin system for the phases ε (hexagonal) and δ (multi-atomic cubic), and here again there is close parallelism between the decrement–composition and the electrical conductivity–composition curves.

VI.—General Conclusions.

Several investigators (Bernal, Dehlinger, Goldschmidt, Hume-Rothery, &c.) have classified the phases present in the copper–tin and copper–zinc systems according to their predominant characteristics,

and have distinguished, in particular, between those which are essentially metallic and those which are homopolar.

CuZn is a typical metallic phase : it is capable of being deformed at high temperatures, and it is associated with a well marked maximum on the electrical conductivity–composition curve. It has a body-centred cubic structure which is perfectly ordered at temperatures below 470° C. The γ phase is entirely different : it is very brittle and its electrical conductivity is little altered by variations in chemical composition. Its unit cell contains 52 atoms and is obviously distorted, because, as Bradley and Thewlis have shown, it can be regarded as having been formed from 27 cells of the β phase with the loss of 2 atoms. It has been suggested by some physicists that in the γ phase the interatomic bonds are of a different type from those in the metals, and more closely resemble those in homopolar bodies. It is interesting to note that these phases are associated with absolute maxima on the modulus–composition curve : this strengthens the view that the modulus is a property related to the atomic linkages.[20] It may be mentioned that the ternary alloy containing copper 53, zinc 30·6, and aluminium 15·3 at.-% has the same type of structure, and a modulus of 16,180 kg./mm.^{2}, and that the γ phase in copper–aluminium alloys[21] has a modulus as high as 20,400 kg./mm.^{2}

It is more difficult to explain the results obtained in the case of the logarithmic decrement. The phenomenon of damping is complex : it is partly due to plastic deformation and partly to intercrystalline thermal currents,[22] but the relative importance of these two sources of internal friction differs in different phases of a single system.

In the δ and γ phases, it appears probable that the plastic effect is negligible : because of their crystalline structure, the propagation of a dislocation must be almost impossible. Generally speaking, irregularity and disorder in a crystal lattice appear to be associated with a low value for the decrement as compared with that for a regular and ordered lattice. This decrease is met with in solid solutions as compared with pure metals, and in the ordered β phase as compared with the somewhat disordered γ phase with its multi-atomic cell. This view is supported by the marked decrease in the internal friction which accompanies an order–disorder transformation.[23]

Acknowledgements.

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MEASUREMENTS ON THE OXIDATION-RESISTANCE OF HIGH-MELTING-POINT ALLOYS.* 1163

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Synopsis.

The resistance to atmospheric oxidation of binary and ternary high-melting-point alloys was investigated at 1250° C. by means of the apparatus described. X-ray and microscopic examinations and Brinell hardness measurements were also carried out, at room temperature.

The alloys of chromium with tungsten and molybdenum form continuous series of solid solutions. The oxidation of the chromium-rich alloys does not differ markedly from that of pure chromium. Alloys with less than 70% chromium have a much higher oxidation rate. This behaviour is due to the formation of the compounds WO_3 or MoO_3, each of which has an appreciable volatility above 1200° C. The consequent evaporation continually exposes new metal surface to attack by air. A similar behaviour was found with the ternary alloys chromium–niobium–tungsten and chromium–tantalum–tungsten. Chromium–tungsten alloys prepared aluminothermically have an oxidation-resistance lower than that of the pure alloys.

In the systems chromium–tantalum (0–70% tantalum) and chromium–niobium (0–60% niobium) two phases, Cr_3Ta_2 and Cr_3Nb_2 respectively, with a wide homogeneous field were found. The oxidation-resistance is highest at the composition of these compounds, which oxidize to one-half to one-third the extent of pure chromium under the same conditions. Chromium–tantalum–niobium alloys on the section Cr_3Ta_2–Cr_3Nb_2 show very irregular behaviour during oxidation, owing to fissure formation at the grain boundaries and peeling away of the oxide layers.

In the range investigated (0–40% niobium) of the nickel–niobium system a compound was found of composition Ni_3Nb. The solubility of niobium in nickel is about 15% at 1250° C. The solubility of nickel in niobium is much less. The oxidation-resistance of the alloys is higher than that of pure chromium only in the niobium-rich portion of the α solid solution. The other alloys, especially near the composition Ni_3Nb, are much less resistant to oxidation.

Some information is also included on the alloys in the ternary section Cr_3Nb_2–Ni.

I.—Introduction.

The object of this work was to investigate the behaviour of binary and ternary alloys in air at temperatures above 1000° C. Alloys of the metals chromium (melting point 1890° C.), tungsten (3400° C.), molybdenum (2620° C.), tantalum (3030° C.), niobium (2415° C.), and nickel (1455° C.) were prepared for this purpose. No work was done on the metals of the platinum group or on titanium or zirconium.

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The paper reports results obtained on the oxidation-resistance of alloys in the systems Cr–W, Cr–Mo, Cr–Ta, Cr–Nb, Cr–Ta–Nb, Cr–Nb–W, Cr–Ta–W, Nb–Ni, and Cr–Nb–Ni. The system Cr–Ta–Ni is discussed in a subsequent paper.[1]

II.—Experimental Methods.

1. *Preparation of Test-Pieces.*

Sintered alloys were unsuitable for oxidation-resistance experiments, as it was difficult to produce sufficiently compact specimens. Oxidation curves of sintered chromium–tungsten alloys were not reproducible. Consequently the alloy test-pieces were made by melting the mixed and pressed metal powders. The following furnaces were used:

(i) An ordinary Tammann furnace with an alumina tube and hydrogen as the protecting gas.

(ii) A graphite electric-resistance furnace, constructed at the Institut, in which the graphite tube was kept in a nitrogen atmosphere during heating, thereby prolonging its life. Before melting the alloy, an alumina tube inside the graphite tube was evacuated several times and swept out with argon, being finally left filled with argon. This alumina tube contained an alumina crucible in which the specimen was placed.

The use of a resistance furnace with a carbon tube is limited to a maximum temperature of 1900° C., since the inner alumina tube will not withstand a higher temperature, and thoria, an alternative refractory, becomes brittle within a few hours owing to reaction with the reducing atmosphere in the carbon tube. Consequently, for the higher-melting-point alloys use was made of:

(iii) A high-frequency furnace with a 3-kVA. valve generator. The test-pieces were melted in a thoria boat without an inner metal tube.

(iv) A furnace in which nine tungsten bars ($275 \times 2 \times 8$ mm.), connected in series, were arranged concentrically round a thoria tube. An input of 10 kW. produced a temperature of 2600° C. in the tube. The pressure inside the furnace could be lowered to 10^{-2} mm. mercury, even at high temperatures.

In all these furnaces the temperature was measured optically through a glass window. Generally the test-pieces were held for about 1 hr. just below the solidus temperature, after initial melting and solidifying.

The metals used were electrolytic chromium, molybdenum powder (" pure for bulbs "), tungsten powder supplied by I.G. Farbenindustrie, tantalum powder (99·5%), niobium powder (86–90%; remainder mainly tantalum, traces of titanium) supplied by Siemens und Halske A.G., and carbonyl nickel.

2. *Examination of the Alloys.*

Since the equilibrium diagrams of the alloy systems investigated were known only in a few cases, some of the missing information had to be supplied. The melting temperatures were determined sufficiently closely for this work by observing the alloys during melting and solidification with an optical pyrometer. It was not possible, however, to determine the liquidus and solidus temperatures exactly by this method. For systems with melting temperatures below 1600° C. ordinary thermal-analysis methods were applied.

Powders of the alloys were prepared by pulverizing or by filing. The specimens were annealed for several hours at about 500° C. below the melting points of the alloys and were examined by X-ray analysis, Debye–Scherrer photographs being taken using chromium or copper radiation. In addition, photomicrographs were taken of polished and etched sections of the alloys.

Brinell hardness was determined with loads of 187·5 and 62·5 kg., with a ball diameter of 2·5 mm. These hardness measurements were taken as a criterion of the mechanical properties of the alloys. Those designated " brittle " broke under test.

3. *Determination of Resistance to Oxidation.*

A simple apparatus was constructed, similar to one used by Portevin, Pretet, and Jolivet.[2] The method entailed the measurement of the decrease of pressure caused by reaction between the alloy and oxygen (and possibly nitrogen) in a closed tube, filled with air. The volume of the tube was such that the difference in pressure after 10 minutes' operation was easily measurable, but no appreciable change in oxygen concentration took place during the test.

A Pythagoras tube (22 × 300 mm.), sealed at one end, was placed with the sealed end in the hot zone of a silicon carbide resistance furnace (Fig. 1). The other end was joined to a water-cooled brass collar carrying a side tube and closed by a tapered brass plug provided with a glass window. The side tube was connected to a barometric-type manometer through a T-type three-way stop-cock, which enabled the furnace tube to be connected (1) to the manometer only, or (2) to the manometer and the outside atmosphere. The furnace was tilted to increase convection inside the tube.

For each determination the polished alloy test-piece (of surface area 1·5–2·5 cm.^{2}) was placed in an alumina boat, pushed into the hot zone of the furnace, and the plug replaced. The atmospheric pressure recorded by the manometer was measured and the three-way tap moved

from position (2) to position (1). Thereafter, the manometer pressure was read after fixed intervals of time, the apparatus being opened to the atmosphere (position (2)) for 1 sec. after each reading.

The temperature of the alumina boat was observed by means of an optical pyrometer (Hartmann and Braun) sighted through the glass window. The pyrometer readings were first checked against those of a platinum/platinum–rhodium thermocouple. Small deviations (mainly due to the absorption of the window) were used to correct subsequent pyrometer readings. The accuracy of the temperature measurements was estimated to be $\pm$ 4° C.

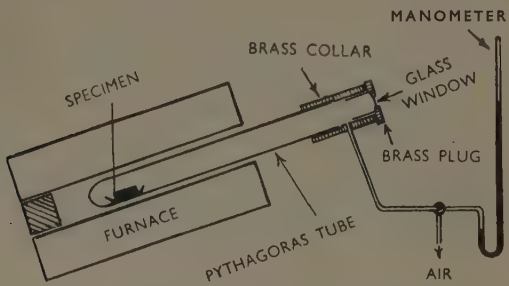

Fig. 1.—Apparatus for Measurement of Oxidation.

The rate of decrease of pressure under the conditions described gives a relative measure of the oxidation rate of the alloys. The attack by air may, of course, cause the formation of nitrides as well. It should be pointed out that with this method there is no means of differentiation between combination with oxygen and nitrogen, and in subsequent discussion of oxidation-resistance, some nitride formation may also be involved.

The possible error in reading the manometer was $\pm$ 0·5 mm. mercury. The alterations in pressure in the tube caused by temperature changes in the furnace ($\pm$ 15° C.) due to fluctuation in voltage, were determined in blank experiments and taken into consideration in correcting the final results. The temperature coefficient of oxidation was also used to correct the final figures. Thus, the maximum error in a single determination on a sample of area 2 cm.^{2}, with a pressure drop of 20 mm. mercury, was calculated to be $\pm$ 7%. The error in the results may actually be higher, owing not so much to inaccuracies in measurement as to variations in soundness of the test-piece. Care was taken not to handle the test-piece, in order to avoid contamination with grease. Generally, the lowest figures of oxidation were taken to be the most correct.

In some cases the increase or decrease in weight of the test-piece due to oxidation was also measured.

III.—Results.

1. *Chromium–Tungsten and Chromium–Molybdenum Systems.*

Details of investigations of the chromium–tungsten and chromium–molybdenum systems, carried out in order to clear up contradictions in

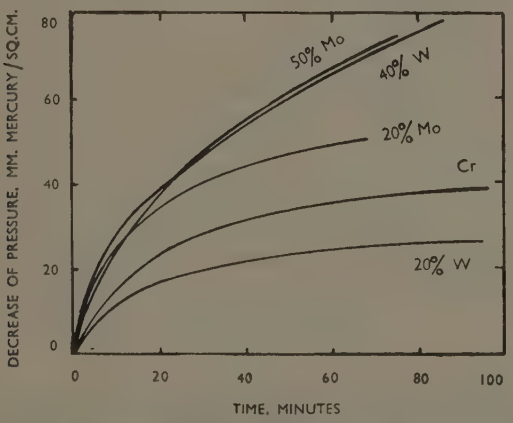

Fig. 2.—Oxidation Rates of Chromium–Tungsten and Chromium–Molybdenum Alloys at 1250° C.

the literature,[3, 4] have already been published.[5] The results indicate an unlimited solubility of chromium in molybdenum and tungsten, at least at higher temperatures. In agreement with previous work, thermal analysis revealed a minimum temperature of melting in both systems, 1720° C. for a chromium alloy containing 30 wt.-% tungsten and 1700° C. for a chromium alloy containing 25 wt.-% molybdenum.

Oxidation of chromium–tungsten and chromium–molybdenum alloys was studied at 1050° and 1250° C. Some characteristic curves of the decrease in pressure with time are given in Fig. 2, the pressure decrease after 40 min. being plotted against composition of the alloys in Fig. 3. Fig. 4 shows the changes in weight of the test-pieces after 60 min. All the values are calculated for 1 cm.^{2} of surface area.

The following deductions can be made from the curves. Alloys with 10–30% tungsten have an oxidation-resistance a little better than that of pure chromium: at higher concentrations of tungsten the oxidation-resistance is not as good as that of pure chromium. In alloys containing

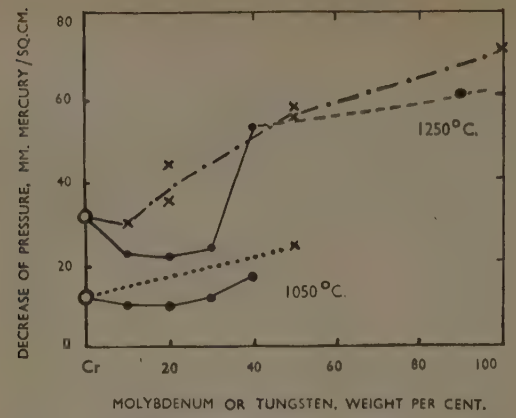

FIG. 3.—Effect of Composition on the Oxidation-Resistance of Chromium–Tungsten and Chromium–Molybdenum Alloys. (Decrease in pressure after 40 min.)

● Chromium–tungsten.
× Chromium–molybdenum.

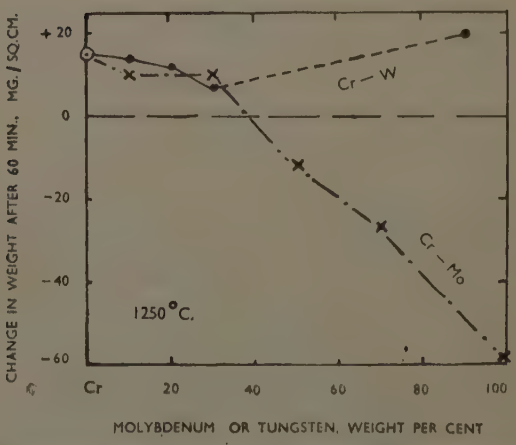

FIG. 4.—Change in Weight of Chromium–Tungsten and Chromium–Molybdenum Alloys after 60 min. of Oxidation.

more than 10% molybdenum the oxidation-resistance is less than that of pure chromium. The increase in weight is less than would be expected from the curves of decrease in pressure. Comparing the corresponding curves in Figs. 2 and 3, it will be seen that they show an increasing divergence as the concentrations of molybdenum and tungsten increase, and at higher concentrations of molybdenum there is even a decrease in weight. This might reasonably be expected, since MoO_3, which melts at 795° C., has an appreciable vapour pressure at 1250° C. Condensed MoO_3 was found in the cooler parts of the tube in the form of white crystals, which were identified by their beautiful display of colours in polarized light.[6] Although WO_3 melts at 1473° C., it has a vapour pressure as high as 9 mm. mercury at 1250° C.[7] Thus, evaporation or sublimation at the temperatures of the experiments explains the discrepancy between the curves of pressure and weight-change. This is also in agreement with the detailed work of Gulbransen and Wysong [8] on the oxidation of tungsten, molybdenum, and some of their alloys. According to this work a loss in weight due to volatilization of the oxides is observed above 475° C. for pure molybdenum, and above 800° C. for pure tungsten.

The high vapour pressures of the oxides MoO_3 and WO_3 are also the cause of the impaired oxidation-resistance of alloys of chromium with molybdenum and higher percentages of tungsten. The evaporation of one component of the oxide layer leaves it in a porous state which facilitates further attack by oxygen in the air. This also explains the form of the curves for 50% molybdenum and 40% tungsten in Fig. 2, which show an increase of oxidation with time approaching linearity. This indicates the formation of non-protective oxide layers. The fact that there is a small decrease in the rate of oxidation is due probably to the partial protection offered by the liquid oxide covering the surface. It was observed occasionally on taking the sample out of the furnace that its surface oxide layer was partly liquid. These alloys appear to be unsuitable for technical applications.

Chromium–tungsten alloys prepared aluminothermically were less resistant to oxidation than the pure alloys. This result, at first surprising, seems to be due to the following factors : (i) chromium–tungsten alloys made by this method are mostly not in a state of equilibrium and may contain a certain proportion of free tungsten.[9] (ii) Dense layers are produced only by γ-Al_2O_3, which is formed at lower temperatures, for instance by anodic oxidation. Above 1000° C., α-Al_2O_3 (corundum) is formed as a porous layer.

Experiments on oxidation of chromium–tungsten alloys produced aluminothermically were also carried out by Isida, Asada, and Higasi-

mura.[10] Their results at 900° C. show a slight increase of the oxidation rate of chromium up to 80% tungsten, and then at higher concentrations of tungsten an accelerated increase of the oxidation rate.

2. *Chromium–Tantalum and Chromium–Niobium Systems.*

No information about the chromium–tantalum and chromium–niobium equilibrium diagrams was found in the literature. Thermal, X-ray, and microscopic analysis of the chromium–tantalum system re-

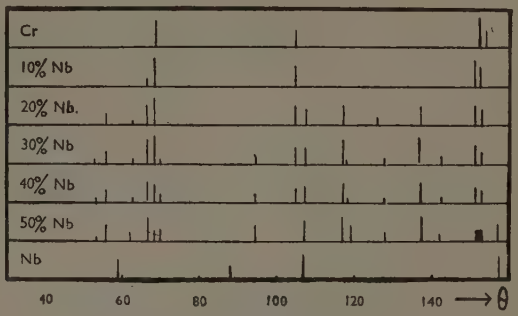

FIG. 5.—Diagrams of the Debye–Scherrer Patterns of Chromium, Niobium, and Chromium–Niobium Alloys.

vealed a phase with a broad homogeneous field extending from about 62% tantalum upwards. This phase which has been assigned the formula Cr_3Ta_2, is formed by a peritectic reaction at 1940° C. The solubility of tantalum in chromium amounts to several per cent., but is certainly below 5%. The diagram, as far as it can be drawn from our results, is reproduced in a subsequent paper.[1]

Difficulty was experienced in producing chromium–niobium alloys, and indeed those containing over 40% of the impure niobium used were so brittle that it was impossible to produce smooth plane surfaces for the oxidation test and microscopic examination. Those which were tested were very similar to the corresponding tantalum alloys. Diagrams of the Debye–Scherrer patterns are given in Fig. 5. The solubility of niobium in chromium also amounts to several per cent. The addition of niobium, however, causes only a slight expansion of the chromium lattice. The appearance of a new phase is shown by Fig. 5 to begin at 20% niobium. Its composition is indicated to be 50–60% niobium. Corresponding as it does to the phase Cr_3Ta_2, it was assigned the formula Cr_3Nb_2. The melting points are about 50°–100° C. lower than in the

system chromium–tantalum, extending from 1750° to 1950° C. for alloys containing up to 50% niobium.

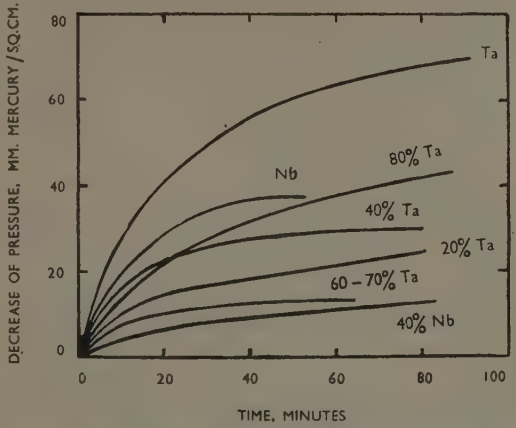

FIG. 6.—Oxidation Rates of Chromium–Tantalum and Chromium–Niobium Alloys at 1250° C.

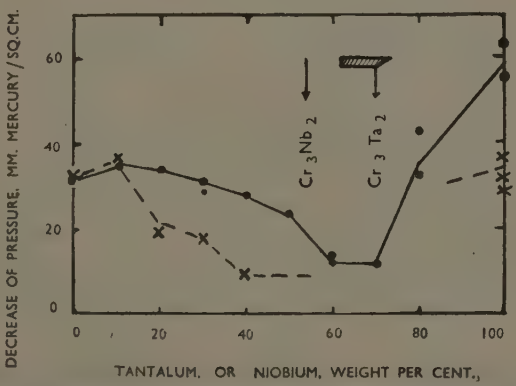

FIG. 7.—Effect of Composition on the Oxidation-Resistance of Chromium–Tantalum and Chromium–Niobium Alloys. (Decrease in pressure after 40 min.)

●——● Chromium–tantalum.
×---× Chromium–niobium.

The oxidation curves for some chromium–tantalum and chromium–niobium alloys at 1250° C. are given in Fig. 6. The decrease of pressure after 40 min. is plotted against composition in Fig. 7. In the α-phase

range the oxidation-resistance of chromium is lowered by additions of niobium or tantalum, but there is an improvement at higher concentrations. The best values are found between 60 and 70% tantalum and above 40% niobium, that is, in the regions of the Cr_3Ta_2 and Cr_3Nb_2 phases. At higher percentages of the added metals the resistance again decreases. The values for pure niobium were found with a 99·5% niobium test-plate. Pure niobium has about the same oxidation-resistance as chromium, but tantalum oxidizes much more easily.

3. *Chromium–Tantalum–Niobium Alloys.*

As an extension of the work on the chromium–tantalum and chromium–niobium alloys, some alloys of the ternary system Cr–Ta–Nb were also tested. Work was carried out on the binary section Cr_3Ta_2–Cr_3Nb_2 since these compositions had proved the best of the binary alloys. Mixtures of the following compositions were heated in the high-frequency furnace to the melting temperatures indicated : 40% niobium, 18% tantalum (1700°–1800° C.); 27·5% niobium, 35% tantalum (1900° C.); 22% niobium, 42% tantalum (1900°–2000° C.); and 16% niobium, 49% tantalum (2000° C.). All these alloys broke under the Brinell test, indicating that they were as brittle as the binary compounds.

The oxidation–time curves were very irregular and difficult to reproduce (Fig. 8). The oxidation rate was high even after 40 min., and was sometimes more rapid at the end than at the beginning. Photomicrographs showed that numerous holes and fissures had developed in the surface during oxidation, and that these defects had permitted an increased attack by air, causing the irregularity in the curves. The decrease in pressure after 40 min. is as great with the ternary alloys as with the binary components Cr_3Ta_2 and Cr_3Nb_2. For the reasons mentioned, however, these values cannot be taken as a reliable criterion of the behaviour of the alloys at high temperatures.

4. *Chromium–Niobium–Tungsten and Chromium–Tantalum–Tungsten Alloys.*

Further tests were carried out to discover whether the beneficial effect of niobium and tantalum on the oxidation-resistance of chromium would be impaired by the presence of tungsten. Two mixtures containing 40% niobium, 18% tungsten, and 27% niobium, 36% tungsten were melted in the high-frequency furnace at 2000° C., forming alloys which were very brittle. The oxidation curves are given in Fig. 9, which shows that the oxide layers give no protection. The progress of oxidation with time is almost linear, and the resulting oxidized surfaces

are rough and cracked. The dotted line in Fig. 9 represents the second treatment of a previously oxidized sample. The oxidation does not

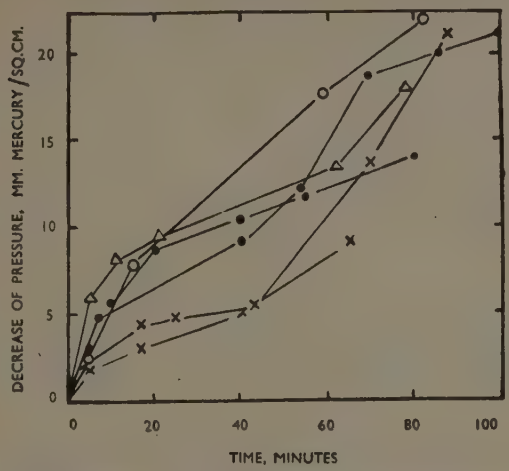

Fig. 8.—Oxidation Rates of Chromium–Tantalum–Niobium Alloys at 1250° C.

● 40% Nb, 18% Ta. ○ 22% Nb, 42% Ta.
× 27·5% Nb, 35% Ta. △ 16% Nb, 49% Ta.

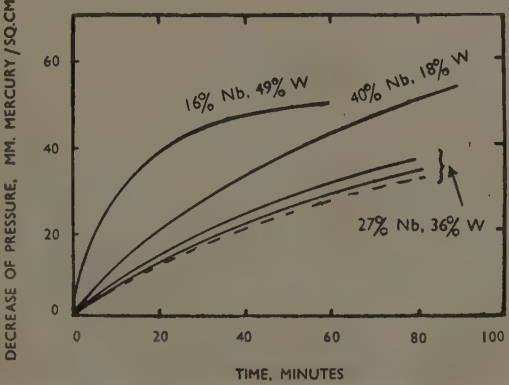

Fig. 9.—Oxidation Rates of Chromium–Niobium–Tungsten Alloys at 1250° C.

differ from that of the first run, owing to the small protection afforded by the oxide layer.

The alloys increased in weight on oxidation. This increase amounted to 10 mg./cm.^{2} after 60 min. for the alloy containing 27% niobium

and 36% tungsten. In comparison with the figures for increase in weight and decrease in pressure obtained with other alloys, this weight increase should have been of the order of 15 mg./cm.^{2} This loss of material can be explained by the evaporation of one component—tungsten, in the form of WO_3, as in the case of the binary chromium–tungsten alloys. In general, therefore, one may expect this behaviour in all alloys containing more than a certain proportion of tungsten. The alloys containing molybdenum show the same effect, but more markedly. These results were also confirmed with two Cr–Nb–W alloys, containing respectively 21% niobium, 43% tungsten, and 16% niobium, 49% tungsten. These were produced by sintering, as their melting points were so high (about 2400° C.). The oxide layers on these alloys also were very porous.

Sintered Cr–Ta–W alloys with 35% tantalum, 35% tungsten, and 52% tantalum, 18% tungsten, respectively, showed similar results. After an 80-min. exposure to air at 1250° C. the test-pieces were almost completely oxidized, the oxides formed covering the remaining metal in the form of a loose powder.

5. *Niobium–Nickel System.*

Since high proportions of tungsten and molybdenum seemed unsuitable for useful alloy formation, the investigations were continued on the basis of the chromium–niobium and chromium–tantalum alloys. These alloys proved to have better oxidation-resistance than chromium, but were very brittle. General experience shows that nickel additions have a beneficial influence on mechanical properties, so in spite of its relatively low melting point, its effect on the alloys with tantalum and niobium was investigated. To this end the binary system niobium–nickel was first studied.

The phase diagram for the system niobium–nickel was known from previous investigations by Grube, Kubaschewski, and Zwiauer [11] and is generally in agreement with the more recent results of Pogodin and Zelikman.[12] Nickel dissolves about 15% niobium at 1250° C. At 35% niobium a compound is formed with the composition Ni_3Nb. The alloys are relatively ductile. The hardness increases with increasing niobium content from 145 Brinell at 3% niobium to 340 Brinell at 33% niobium. The eutectic temperature in this range is 1265° C. The nickel-rich alloys were produced by the reduction of Nb_2O_5–Ni powder mixtures with highly purified hydrogen. Niobium-rich alloys with 5, 10, and 20% nickel were melted *in vacuo*. Photomicrographs revealed a solubility of nickel in niobium of less than 5%.

The oxidation rate of the alloys was much lower than would conform

to a parabolic law. This is explained by the nature of the oxide layers formed on the niobium-rich alloys. They are very dense, corresponding to the high ratio of the molecular volume of the oxide to the atomic volume of niobium. They easily flaked off the cooled test-pieces at a slight blow. This may be due to the high differential contraction of the metal and oxide layer on cooling. Such layers would break off easily on mechanical treatment and would permit a renewed attack on the

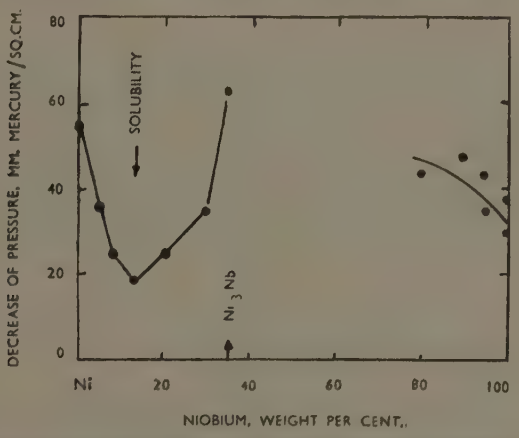

FIG. 10.—Effect of Composition on the Oxidation-Resistance of Niobium–Nickel Alloys. (Decrease in pressure after 40 min.)

surface by air. In nickel-rich alloys this characteristic is not so pronounced owing to the smaller volume ratio. The oxidation, moreover, obeys more closely the parabolic law.

The oxidation rate of the nickel-rich α phase is lower than that of pure nickel (Fig. 10). Alloys with 5–13% niobium have a lower oxidation rate than has pure chromium. In the heterogeneous field ($\alpha + Ni_3Nb$) the oxidation-resistance decreases and at 35% niobium becomes lower than that of nickel. The oxidation-resistance of pure niobium is approximately the same as that of chromium. Additions of 5–20% nickel lower this resistance.

6. *Chromium–Niobium–Nickel Alloys.*

Further tests with alloys containing tantalum revealed relatively good results over a certain field in the Cr–Ta–Ni system. The results extend the information on oxidation-resistance and phase relationships

to the binary border systems as well as over the ternary system. This is discussed in a separate paper.[1]

General experience shows that corresponding alloys of tantalum and niobium are very similar in properties. Since alloys containing niobium have lower melting points and proved to be more brittle (owing possibly to the lower purity of the metal supplied), only a few alloys of the ternary system Cr–Nb–Ni were produced. Less value is attached to results obtained with these than to those obtained on the Cr–Ta–Ni system.

Five alloys of the section Cr_3Nb_2–Ni were melted in argon : (1) 22% niobium, 60% nickel; (2) 27% niobium, 50% nickel; (3) 38% niobium, 30% nickel; (4) 44% niobium, 20% nickel; (5) 49% niobium, 10% nickel.

Alloys (3), (4), (5) were very brittle; (1) and (2) could be split only with hammer and chisel. The melting points are about 300° C. less than those of the corresponding tantalum alloys. The oxidation rate of Cr_3Nb_2 is not appreciably influenced by additions of nickel, but the oxide layers do not adhere so strongly.

ACKNOWLEDGEMENT.

The authors are indebted to Mr. E. Ll. Evans, B.Sc., who has kindly suggested alterations to the English script.

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OXIDATION-RESISTANCE AND SOME PHASE RELATIONSHIPS IN THE SYSTEM CHROMIUM–TANTALUM–NICKEL.* 1164

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Synopsis.

A preliminary investigation of the constitution of the systems chromium–tantalum, nickel–tantalum, and chromium–tantalum–nickel has been carried out, using thermal, microscopic, and X-ray methods.

In the system chromium–tantalum an intermediate phase exists, having a broad homogeneous field extending from about 62% tantalum towards the tantalum-rich compositions. This phase, which is designated Cr_3Ta_2, is formed peritectically at 1940° C. The solid solubility of tantalum in chromium amounts to several per cent.

In the system nickel–tantalum two phases were found, of compositions approximating to Ni_3Ta and Ni_2Ta_3; the first of these has a melting-point maximum at 1540° C., while the second is formed peritectically at 1525° C. The solubility of tantalum in nickel is 30% at 1000° C.

In the ternary system chromium–tantalum–nickel the two binary phases Cr_3Ta_2 and Ni_3Ta possibly form a continuous series of solid solutions. The field Cr–Ni–Cr_3Ta_2–Ni_3Ta is therefore governed by the three eutectics of the border systems, which meet at a ternary eutectic point at 37% chromium, 46% nickel, 17% tantalum, and 1165° C. The solubility of the other components in chromium is small, while that in nickel is relatively high.

Results of high-temperature oxidation tests on the systems nickel–tantalum and chromium–tantalum–nickel are given. Alloys with a relatively high oxidation-resistance are found in the range 10–40% tantalum, 50–80% nickel, and 10–25% chromium. The Brinell hardness of these alloys is 150–350 at room temperature and the solidus temperatures lie within the range 1250°–1380° C. The oxidation-resistance of an alloy containing 25% tantalum and 62·5% nickel, for instance, is about ten times higher than that of chromium and three times higher than that of the commercial alloy Thermax 11, at 1250° C. The alloys in the concentration range 45–56% tantalum, 25–50% nickel, and 5–40% chromium have a higher solidus temperature, and while their oxidation-resistance is lower than in the first-mentioned range, it is still twice as good as that of pure chromium.

The oxidation properties can be improved by small additions of less noble metals. Good results were obtained by adding up to 1 or 2% of calcium, thorium, silicon, or beryllium.

I.—Introduction.

In a previous paper [1] several alloys of the high-melting-point metals chromium, tungsten, molybdenum, tantalum, niobium, and nickel, were examined with particular reference to their oxidation-resistance. It

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was found that the ternary Cr–Ta–Ni alloys had the most favourable properties. Alloys containing tungsten and molybdenum were too unstable in contact with air owing to the volatilities of their respective trioxides. Alloys of niobium have oxidation properties similar to, but lower melting points than, the corresponding tantalum alloys.

As an extension of this preliminary work an investigation has been carried out of the oxidation-resistance of alloys of the ternary Cr–Ta–Ni system and its associated binary systems. This has been conducted in more detail than the previous work, as it is believed that this is the system likely to provide the most useful high temperature oxidation-resistant alloys. A further improvement of the Cr–Ta–Ni alloys by small additions will almost certainly prove possible.

Thermal, X-ray, and microscopic analyses of the alloys in these systems were carried out to supplement the measurements of resistance to oxidation. The phase relationships are only roughly determined, however, and further work is necessary to establish them with any accuracy.

The metals used were tantalum powder (99·5% Ta) supplied by Siemens und Halske A.G., carbonyl nickel powder, and electrolytic chromium which was powdered in a mortar to a grain-size less than 0·09 mm. The weighed powders were mixed and pressed. The weight of each test-piece was 15 g.

II.—Chromium–Tantalum System.

The melting points of the chromium–tantalum alloys are too high to permit the use of thermocouples for thermal analysis, so temperatures were measured optically. Temperatures determined were those of primary crystallization during cooling and beginning of melting on heating.

Alumina was used for the boat and furnace tube for alloys containing 0–50% tantalum, and thoria for alloys containing higher percentages of tantalum. X-ray measurements were carried out in addition to the thermal analysis, and the preliminary results are shown in Fig. 1.

The solubility of tantalum in chromium could not be measured by X-ray methods, as there is only a very slight expansion of the lattice, despite the larger atomic radius of tantalum compared with chromium. The solubility was estimated from microscopic examination to be less than 5%. The following facts were established:

(*a*) Additions of tantalum lowered the melting point of pure chromium, which was observed to be 1840° C. This temperature is probably a little low.*

* Grube and Knabe [2] found 1850° ± 10° C.

(*b*) The liquidus curve from the chromium side meets the horizontal eutectic line at 34% tantalum and 1700° C.

(*c*) At about 62% tantalum the homogeneous field of a new phase appears. (The microstructure of the 60%-tantalum alloy still shows a small amount of eutectic at the grain boundaries.) This phase was designated Cr_3Ta_2; the alloy corresponding to this composition is very brittle. Microscopic examination of an untreated fractured surface at a magnification of 1100 dia. revealed that small crystals had been torn

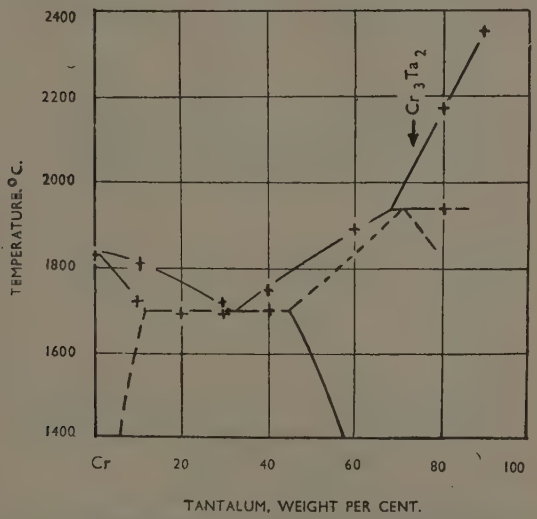

Fig. 1.—Equilibrium Diagram of the System Chromium–Tantalum.

out leaving cavities of a regular hexagonal form. One of these is shown in Fig. 5 (Plate XLIII). A Debye–Scherrer powder photograph showed that the alloy might have a hexagonal close-packed structure. An alternative, tetragonal structure was ruled out by the microscopic observation. Thermal analysis showed the formation of Cr_3Ta_2 to take place peritectically at 1940° C.

III.—Nickel–Tantalum System.

An investigation of this system was carried out by Therkelsen,[3] who determined the solidus and liquidus temperatures optically. Further work, employing X-ray methods, was done by Wallbaum,[4] who discovered a compound Ni_3Ta which undergoes transformation at 1350° C.

Alloys were prepared of compositions ranging from 0 to 90% tanta-

lum in steps of 5%. These were heated in a Tammann furnace to above their melting points, in an atmosphere of carefully purified argon. They were stirred with the thermocouple sheath for ¼ hr., allowed to solidify, and held for 1 hr. at just below the solidus temperature. The transition points were observed during heating and cooling, using a thermocouple calibrated at the melting points of gold, silver, and nickel.

The thermal effects observed were used in constructing the equilibrium diagram (Fig. 2).

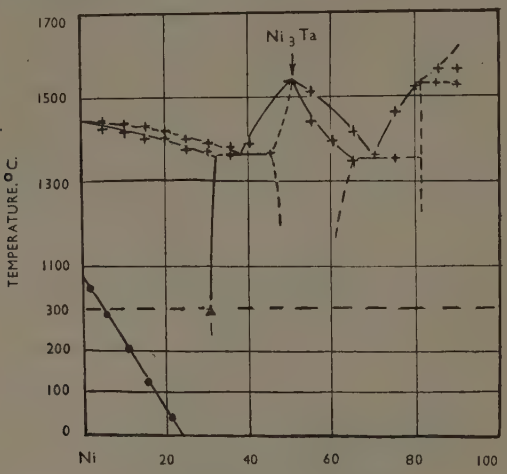

Fig. 2.—Equilibrium Diagram of the System Nickel–Tantalum.

X-ray analysis showed an expansion of the face-centred cubic nickel lattice up to 30% tantalum. For this analysis the alloys were heated to 1000° C. and quenched, so that the solubility mentioned corresponds roughly to that temperature. The lattice parameter of the saturated solid solution is 3·594 Å.

The positions of the Curie points of the solid solution are also given in Fig. 2, and show that alloys containing more than 22% tantalum are paramagnetic at room temperature.

At approximately 50% and 80% tantalum, two intermetallic compounds exist, which may be designated Ni_3Ta and Ni_2Ta_3, respectively. The first is distinguished by a maximum in the melting point at 1540° C.; the second is formed peritectically at 1525° C. The low rate at which equilibrium is attained, as well as the multiplicity of lines in the Debye–

Scherrer photographs, did not permit of the exact definition of the phase boundaries.

Ni_3Ta forms eutectics with the nickel solid solution at 38% tantalum and 1365° C., and with Ni_2Ta_3 at 70% tantalum and 1350° C.

A transformation below the eutectic temperature: $Ni_2Ta_3 \longrightarrow Ni_3Ta$ mentioned by Therkelsen,[3] and a transformation of the Ni_3Ta phase at 1350° C. observed by Wallbaum,[4] were not confirmed in this work. The alloy containing 70% tantalum, for instance, has only one arrest (the eutectic point) on its cooling curve, and that containing 50% tantalum has an arrest only at the melting temperature of Ni_3Ta.

IV.—Chromium–Tantalum–Nickel Alloys.

Six sections of the ternary system were selected for thermal analysis: three parallel to the nickel–chromium side with 10, 20, and 50% tantalum, and three parallel to the nickel–tantalum side with 10, 20, and

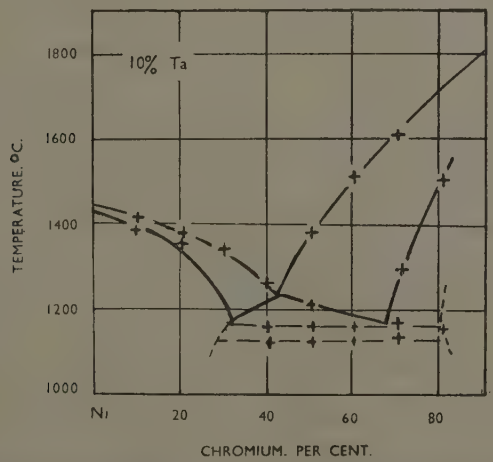

Fig. 3.—The 10%-Tantalum Section of the System Chromium–Tantalum–Nickel.

40% chromium. In all, 33 alloys were examined. No attempt was made to examine alloys containing more than 50% tantalum, as these were too brittle to be of technical importance.

The cooling curves of all the alloys were first determined. The thermal effects, some of which were small, required the use of a differential method. Next to the ordinary thermocouple a differential thermocouple was introduced into the molten alloy. It consisted of two platinum wires (0·3 mm. dia.) joined by a 12 mm. piece of platinum–

rhodium wire of the same dia., arranged so that one connection dipped into the molten metal, while the other remained just above the surface. By this method quite small thermal arrests were observed. The main purpose of these measurements was to determine the solidus temperatures, in order to fix the upper limit of technical application of the alloys. In Fig. 13, which will be discussed more fully later, the solidus temperatures are shown by dotted lines. In addition, the concentration and temperature of the eutectic point and the extent of the three phase fields in each of the sections were determined. Fig. 3 shows the section parallel to the nickel–chromium side containing 10% tantalum. A considerable decrease in the melting-point temperature to the eutectic temperature (1165° C.) may be noted. There is another transformation horizontal 35° C. below the eutectic temperature. This probably indicates a polymorphic transformation.

Occasionally, on annealing an alloy near its eutectic temperature, a rise in temperature occurred and a molten portion separated from the solid test-piece. This melt, which should have been of eutectic composition, was found by chemical analysis to contain nickel 45·7, chromium 36·7, and tantalum 16·9%, a composition which agreed with the results of thermal analysis.

Two sections originating at the chromium corner were examined by X-ray methods (using a chromium anode) to supplement the thermal-analysis results. The alloys were prepared in the usual way, then the samples were powdered, annealed for 2 hr. at 900° C. and quenched. It was found that the lattice parameter of the body-centred cubic chromium lattice does not vary with the concentration of the added metals. Pure chromium has a parameter of 2·878 Å, while the alloy containing chromium 98, tantalum 1, and nickel 1% has a parameter of 2·879 Å. Alloys containing a higher percentage of added elements have lattice parameters of an average value of 2·880 Å, independently of whether they are cooled quickly or slowly. The deviations do not exceed the experimental error. A very low solubility of tantalum and nickel in chromium is indicated.

Similar tests were carried out on two sections (chromium-rich and tantalum-rich) in the nickel corner of the system, a cobalt anode being used in this case. The lines of the nickel lattice alone appeared in all the X-ray photographs except that of the alloy containing 55% nickel and 15% tantalum. In Fig. 4 the lattice parameters are plotted against atomic percentage. The limiting values of the solubilities of chromium and tantalum in nickel can be derived from these curves. There was no difference in the lattice constant of alloys cooled slowly or quickly from 1160° C.

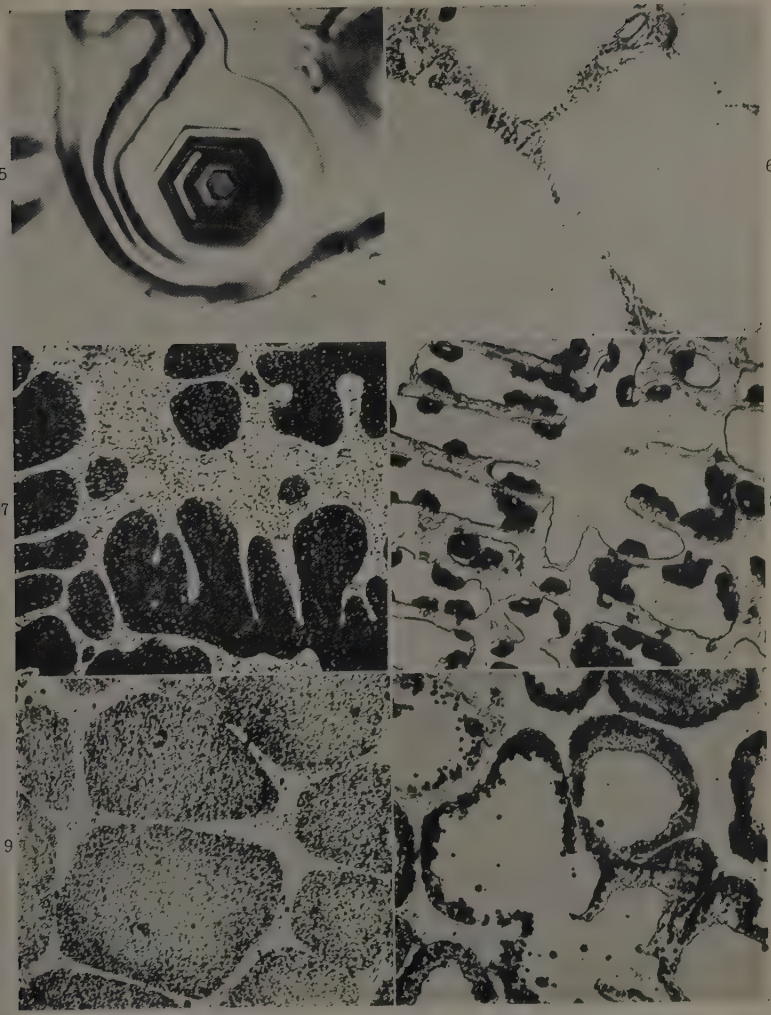

FIG. 5.—Fractured Surface of Alloy with 30% Chromium, 70% Tantalum. Oil immersion. × 1100.

FIG. 6.—Alloy Containing Chromium 20, Nickel 30, Tantalum 50%, Annealed 100 hr. at 1350° C. Etched with *aqua regia*. × 100.

FIG. 7. -Alloy Containing Chromium 60, Nickel 30, Tantalum 10%, Annealed 100 hr. at 1000° C. Etched with *aqua regia*. × 200.

FIG. 8.—Alloy Containing Chromium 60, Nickel 30, Tantalum 10%, Annealed 20 hr. at 1150° C.; quenched. Etched with *aqua regia*. × 200.

FIG. 9.—Alloy Containing Chromium 70, Nickel 20, Tantalum 10%, Annealed 100 hr. at 1000° C. Etched with *aqua regia*. × 200.

FIG. 10.—Alloy Containing Chromium 70, Nickel 20, Tantalum 10%, Annealed 20 hr. at 1150° C.; quenched. Etched with *aqua regia*. × 200.

[*To face p. 122.*

The alloys analysed thermally were also examined microscopically. Long annealing periods were required for the establishment of equilibrium. Only those alloys of low tantalum content attained complete equilibrium, and it could not be reached with alloys containing more than 50% tantalum, even after annealing for 200 hr. at 1100° C.

Fig. 6 (Plate XLIII) shows the photomicrograph of an alloy with 50% tantalum and 30% nickel. Even after annealing for 100 hr. at 1350° C. the alloy is not completely homogeneous. Unfortunately, the vapour pressure of chromium is relatively high at these temperatures; some test-pieces, enclosed in silica tubes and annealed for 100 hr. at 1000° C. *in vacuo*, showed considerable sublimation of chromium. At still higher temperatures sublimation could not be suppressed even in argon.

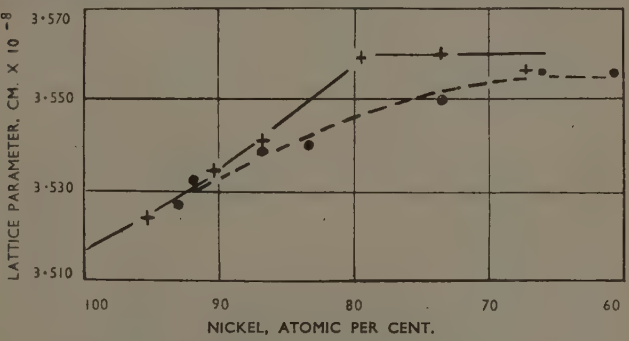

FIG. 4.—Lattice Parameters of Alloys in the Nickel Corner of the System Chromium–Tantalum–Nickel.

The transformation at 1130° C. already discussed in connection with Fig. 3 can also be detected in the photomicrographs of the alloys with 30% nickel, 60% chromium, and 20% nickel, 70% chromium. Figs. 7 and 9 (Plate XLIII) show the alloys after annealing at 1000° C. for 100 hr.; Figs. 8 and 10 (Plate XLIII) show the same alloys after 20 hr. annealing at 1150° C. and quenching in water. The beginning of the transformation, which is arrested by quenching, is clearly recognizable at the grain boundaries. It will be noted that the phase stable above 1130° C. is more resistant to chemical attack, the aqua regia having very little effect on the crystals, which etch very darkly after annealing. No transformation was observed during these experiments in the nickel–chromium system, so that this transformation may be that of the Cr_3Ta_2 phase. It was observed during thermal analysis over the whole of the range in which this compound occurs.

The following general deductions may be made concerning the form

of the ternary equilibrium diagram. The system appears to be of a ternary eutectic form, the eutectic composition being nickel 46, chromium 37, tantalum 17%, and its melting point 1165° C. In the tantalum corner there is a broad homogeneous field which possibly includes the phases Ni_3Ta and Cr_3Ta_2. In the nickel corner there is a broad homogeneous field corresponding to a solubility in nickel of 30% each of chromium and tantalum. Only a small solubility region is found in the chromium corner.

V.—Resistance to Oxidation.

The apparatus and method used for the determination of resistance to oxidation have been described in a previous paper.[1] The decrease in pressure due to the reaction of the test-piece with air in the closed apparatus is measured by a manometer. The apparatus is operated so as to observe the progress of oxidation with time. In Fig. 11 several experimental curves are given which show the change of pressure (mm. mercury) with time, the pressure change being calculated for unit area (1 cm.^{2}) of the test-piece. These values are relative only, and hence for comparison the curve for pure chromium is included. The parabolic law of surface oxidation is seen to hold only in a few cases.

The oxidation-resistance of the binary border systems was first investigated. The results on the chromium–tantalum system have already been reported.[1] The variation of rate of oxidation with composition in the nickel–tantalum system is shown in Fig. 12. The total decrease in pressure after 40 min. operation of the apparatus is taken as a measure of the oxidation rate. The trend is similar to that of the nickel–niobium alloys. Beginning from the nickel end, there is a progressive decrease in the oxidation rate in the nickel-rich α phase down to one-half the value for pure chromium (at 10% tantalum); an increase in rate in the next, heterogeneous region up to the composition Ni_3Ta; finally, an accelerated increase as far as the alloy containing 78% tantalum. Thus the alloys containing between 20% and 78% of tantalum are less resistant to oxidation than is pure chromium. The oxide layers formed, however, afford good protection and the reaction with air at 1250° C. virtually ceases after 40–60 min. The oxidation of the alloys containing 60–70% tantalum proceeds parabolically with time, while the oxidation of the other alloys diminishes more quickly than would correspond to this law.

The oxidation behaviour of the chromium–nickel alloys being so well known, the authors deemed it unnecessary to carry out any work on that system. The rates of oxidation between 700° and 1100° C. were determined by Matsunaga [5] by measuring changes in weight. In order to use these values in Fig. 13, the ratio between Matsunaga's change in

weight and the authors' change in pressure was determined for pure chromium and nickel, and the values for the binary system were calculated proportionally. This method, though not exact, is adequate for comparison purposes.

The data for the ternary Cr–Ta–Ni alloys are summarized in Table I, which includes the composition of the alloys, their solidus temperatures as far as they are known, and Brinell hardness numbers as a measure

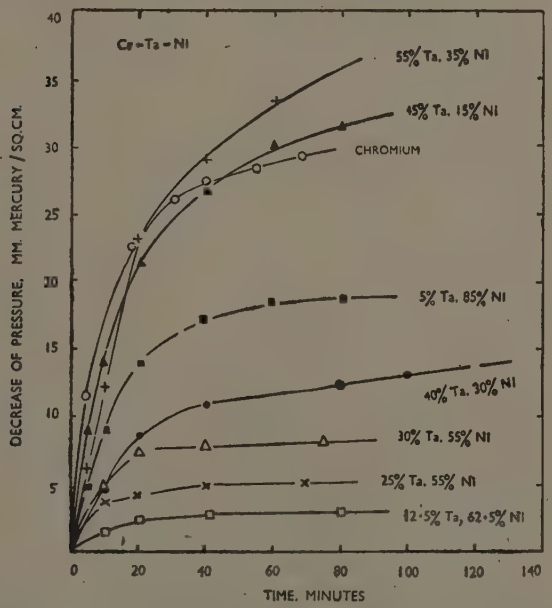

FIG. 11.—Oxidation Rates of Chromium–Tantalum–Nickel Alloys.

of their mechanical behaviour at room temperature. Those termed "brittle" fractured in the Brinell machine (load 187·5 kg.). Again the decrease in pressure after 40 min. attack by air at 1250° C., calculated for 1 cm.^{2} area of test-piece, is taken as a relative measure of resistance to oxidation. Comparison may be made between the various alloys, pure nickel, chromium, and tantalum, and the industrial alloy * "Thermax 11". Each oxidation figure is an average of several determinations, and where the disparity was great, the limits are given in Table I. The final column gives the decrease in pressure per unit area during the 10

* Deutsche Edelstahlwerke, Krefeld.

TABLE I.—*Properties of Chromium–Tantalum–Nickel Alloys.*

No.	Composition.		Solidus Temp., ° C.	Brinell Hardness, kg./mm.²	Decrease in Pressure, mm.Hg/cm.²	
	Tantalum, wt.-%.	Nickel, wt.-%.			After 40 min.	During the 10 min. following the initial 40-min. treatment.
1	2·5	2·5	...	...	21	...
2	3·4	90	1420	145	16	0·5
3	5	85	1410	...	17	0·4
4	6·8	13·2	1165	650	(20)	1·8
5	6·6	90	1420	...	14	0·8
6	10	70	1330	179	6	0·3
7	10	80	1380	135	7	0·3
8	10	85	1410	...	17	0·4
9	12·5	62·5	1230	201	3	0·1
10	13·2	6·8	1350	470	23	...
11	15	25	1165	632	(13)	3·3
12	15	55	1190	390	12	0·1
13	20	10	1410	750	14	...
14	20	70	1320	200	7	0·1
15	25	25	1165	611	(28)	1·5
16	25	45	1200	...	17	0·7
17	25	56	1260	393	5	0·1
18	25	62·5	1290	332	3	0·05
19	30	25	1200	653	(17)	1·7
20	30	30	1165	555	14	0·7
21	30	55	1280	...	8	0·1
22	30	60	1310	315	7	0·05
23	35	50	1280	246	8	0·4–0·8
24	40	20	1440	438	31	0·2–1·5
25	40	30	1300	750	10	0·3
26	40	35	1250	635	17–22	0·1–0·5
27	40	50	1310	280	5	0·1–0·2
28	42	40	1275	341	11	0·6
29	45	15	1500	650	27	1·1
30	45	25	1430	507	17	1·0
31	45·5	35	1310	538	19	0·5
32	45	45	1320	390	9–13	0·2–0·8
33	50	10	1600	brittle	24	1·2
34	50	20	1570	brittle	24	0·4
35	50	30	1480	560	13	0·4–1·0
36	50	35	1370	632	16	1·2
37	52	29	1540	brittle	18	0·3
38	53	25	1580	brittle	17	0·8–1·6
39	55	35	1550	555	15–(34)	1·2
40	56	20	...	brittle	10–16	0·9
41	56	37·5	1560	653	12	0·5
42	59	20	...	brittle	19	0·5
43	60	25	...	brittle	...	...
44	62·5	20	...	brittle	...	...
45	68	25	...	brittle	40	0·4
46	70	17·5	1850	brittle	16	1·0
47	72	20	...	brittle	21	1·0
48	74	10	...	brittle	...	...
49	Chromium		1850	180	28	1·0
50	Nickel		1455	80	57	0·5
51	Tantalum		3030	...	59	2·5
52	Thermax 11		...	...	9	0·05

min. following the initial 40-min. treatment. Low figures indicate a flattening of the oxidation–time curves (cf. Fig. 11), and the formation of highly protective oxide layers. Protection may be regarded as "good" for figures below 0·5, and "hardly sufficient" for figures between 0·5 and 1. Alloys having values exceeding 1 in this last column oxidize fairly rapidly after a moderately long, further period of treatment, as, for example, alloys 4, 11, 19, and pure tantalum. Low values in the final column are found with alloys 9, 12, 14, 17, 18, 21, 22, and Thermax 11. The behaviour of the alloys in the first 40 min. suggests that alloys 9

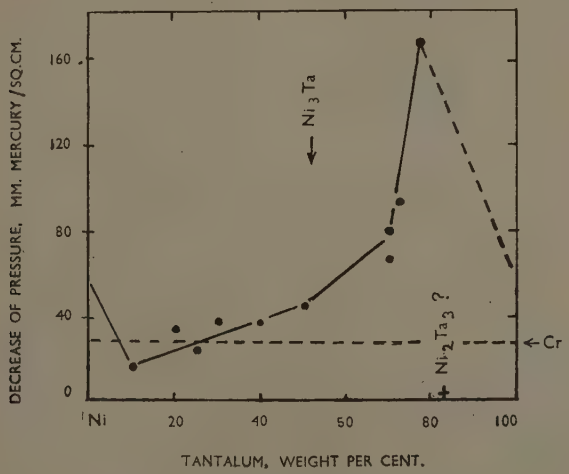

FIG. 12.—Effect of Composition on Oxidation-Resistance of Nickel–Tantalum Alloys. (Decrease in pressure after 40 min.)

and 12 are three times more resistant than Thermax 11. Nearly all the ternary alloys tested have a better resistance to oxidation than has pure chromium.

A clearer picture of the results obtained is given by Fig. 13, which also includes the measured or calculated values for the binary alloys. The dotted lines show the solidus temperatures. The alloys investigated are indicated by crosses or other symbols. The key under the Figure shows the hardness of the alloys under the Brinell test, while those which broke under this test are represented by crosses. The adjacent numbers show the relative rates of oxidation as given in Table I. Brackets round the numbers indicate a continued appreciable rate of oxidation after the initial 40 min. This behaviour is due probably to the forma-

tion of brittle, badly adhering oxide layers, whose continual disruption results in very slight diminution of the rate of attack by air with time.[6]

As an example of the data obtainable from Fig. 13, the alloy containing tantalum 25, nickel 62·5, and chromium 12·5% has a Brinell

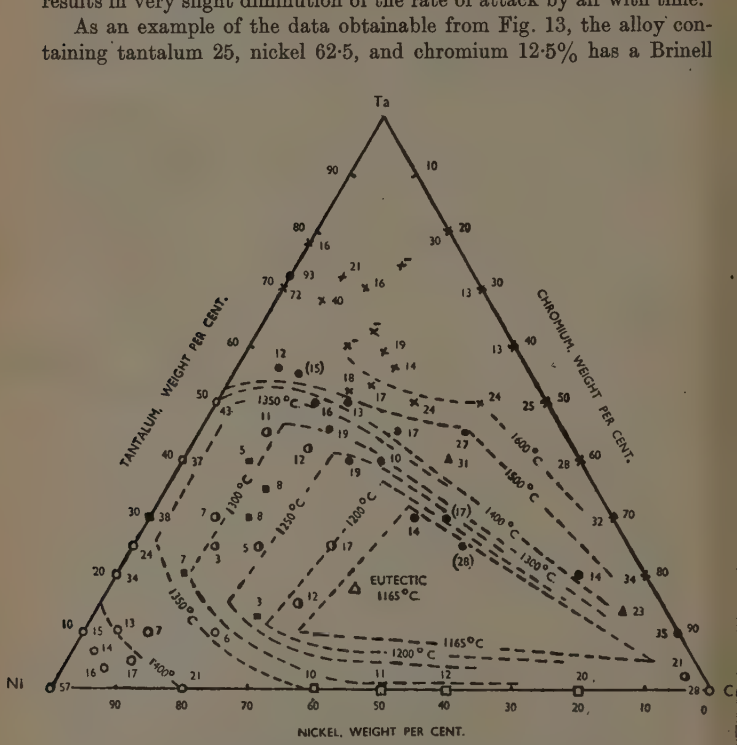

FIG. 13.—Oxidation-Resistance, Hardness, and Solidus Temperatures of Chromium–Tantalum–Nickel Alloys.

The numbers give the decrease in pressure (due to absorption of oxygen and nitrogen) in mm. Hg/cm.^{2} after 40 min. at 1250° C. Brackets round the numbers indicate a relatively high rate of decrease in pressure at the end of the 40-min. treatment (cracked or otherwise unsound oxide layers).

KEY.

×	Brittle
●	Brinell hardness > 500
▲	" " 400–500
◑	" " 300–400
■	" " 200–300
○	" " < 200
□	" " not observed
- - -	Solidus temperature.

hardness at room temperature of 300–400 kg./mm.^{2}, it is completely solid below 1290° C. and its resistance to oxidation at 1250° C. is about ten times higher than that of pure chromium (and about three times that of Thermax 11). This is regarded as the best alloy of the system. In all cases the temperature of oxidation was 1250° C., which is above the solidus temperature of some of the alloys. Notwithstanding the fact that some of these alloys were partially liquid, their oxidation data have been included in Fig. 13 for purposes of comparison.

It is shown in Fig. 13 that alloys in the range 10–40% tantalum, 50–80% nickel, and 10–25% chromium have good resistance to oxidation.* The Brinell hardness of these alloys is between 150 and 300, and their solidus temperature is between 1250° and 1380° C. Alloys with quite good resistance to oxidation and with greater hardness and higher solidus temperatures are found with higher contents of tantalum, namely in the concentration range 45–56% tantalum, 25–50% nickel, and 5–30% chromium. In this range solidus temperatures are 1350°–1600° C., and the hardness exceeds 400 units. Those alloys containing over 50% tantalum which were tested proved to be too brittle to allow any machining or mechanical working. Moreover, the mechanical properties and oxidation-resistance of alloys containing more than about 35% chromium show that they are unsuitable for practical purposes.

Various elements have been quoted as improving oxidation-resistance when introduced in small quantities. For instance, the alkali and alkaline-earth metals, aluminium, lanthanum, silicon, cerium, and thorium are said to improve the oxidation-resistance of nickel.[8] An examination was made of the effect of some of these elements on the oxidation-resistance of an alloy containing tantalum 42, nickel 40, and chromium 18%. The oxidation rate was increased by adding up to 2% of sodium or magnesium. Additions of silicon, calcium, thorium, and cerium are beneficial. An addition of 1% calcium doubled the resistance of the alloy. Beryllium additions also improve the resistance. It may be supposed that these additions will have a similar influence upon the other Cr–Ta–Ni alloys, so that it should in general be possible to improve their oxidation properties by making small additions.

VI.—Conclusions.

The work described was intended not so much to produce alloys of direct technical application, as to obtain systematic information on the behaviour of alloys of the high-melting-point metals, and in doing

* Stahlwerke Roechling–Buderus A.G. and A. Kropf recommend age-hardening alloys with 0–40% chromium, 3–50% tantalum, 0·1–1% carbon, 40–60% nickel for producing stainless, heat-resisting, and hard surgical instruments.[7]

so to assist further work on oxidation-resistant materials. From among the binary and ternary systems investigated, alloys falling within part of the Cr–Ta–Ni system prove to be the most useful and may be used as a basis for further development. This would entail the study of the effect of small additions of various other elements. Improvement is required not only in oxidation-resistance, but also in what is perhaps more important, the mechanical strength at high temperatures. Information kindly provided by Dr. W. Rohn (Heræus Vakuumschmelze, Hanau, Germany) suggests that the mechanical properties of the best of the alloys discussed are unsatisfactory. The development of oxidation-resistant alloys with good all-round mechanical properties above 1250° C. appears to be very difficult. The solution may lie in the use of a material of the requisite mechanical strength, coated or plated with an oxidation-resistant alloy. Experiments on these lines have been carried out by Bückle,[9] whose paper on the subject contains some encouraging results.

ACKNOWLEDGEMENT.

The authors are indebted to Mr. E. Ll. Evans, B.Sc., who has kindly suggested alterations to the English script.

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NON-METALLIC INCLUSIONS IN MAGNESIUM-BASE ALLOYS AND THE FLUX-REFINING PROCESS.* 1165

By E. F. EMLEY,† B.Sc., Member.

Synopsis.

This paper records the results of an investigation into the behaviour of inclusions in molten metal and the nature and function of the process of refining with an inspissated flux.

Attempts to contaminate magnesium alloys with oxide and flux, a study of experimental systems of transparent immiscible liquids whose physical properties resemble those of metal and flux, and the application of Stokes' law to the settling of flux inclusions under gravity have led to certain conclusions concerning the behaviour of inclusions in a body of molten metal and the essential function of a refining flux, which are considerably at variance with published information. In particular it is concluded, contrary to general belief, that inclusions of oxide or flux found in castings do not arise from oxide or flux suspended in the body of the molten metal prior to pouring, whether or not any flux-refining process has been employed, but that inclusions can arise at the time of casting from numerous causes which are considered. Chloride inclusions can also arise in sand castings through sucking of an external chloride film into areas of outcropping microporosity during solidification.

The essential function of an inspissated flux is not to remove suspended impurities from the metal during the refining process, but to provide a cover on the metal of suitable physical properties to enable a clean stream of metal to be poured. Stirring the inspissated flux into the metal reduces the risk of flux inclusions arising at the time of pouring from abnormal conditions or careless procedure. The chemical nature of the inspissated flux is of secondary importance, provided that the constituents are inert to magnesium and the mixture possesses suitable physical properties. These properties are discussed, and indications are given of the ways in which some desirable properties may be obtained and certain defects avoided.

Methods are described for detecting inclusions and for determining their origin by chemical, microscopic, and spectroscopic means.

I.—Introduction.

This paper deals with the origin of non-metallic inclusions in commercial or "standard" ‡ magnesium alloys, with the nature of the refining action of inspissated fluxes, with methods for the detection of inclusions, and with the examination of particular inclusions so as to determine the cause of their occurrence. Particular attention is directed to chloride-containing inclusions in view of the serious corrosion to which these can give rise on exposure to air. The subject of non-metallic inclusions in

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‡ This term is used for convenience to denote pure magnesium and its commercial alloys containing aluminium, zinc, or manganese.

magnesium alloys containing zirconium, which is a matter of special metallurgical interest, is discussed in a later paper.[26] The effects of inclusions on the mechanical properties and corrosion-resistance of alloys are also considered in the later paper.

Until fairly recently there has been little published information on the properties and use of fluxes for magnesium alloys and even less dealing with their mode of action. The history of the development of fluxing methods in Germany has been outlined by Beck,[1] and methods in use in various countries by 1937 are described in French Air Ministry Reports.[2] More recently, recommended melting and fluxing procedures have been given by Emley[3] and Nelson.[4] Much otherwise unpublished information on the composition and properties of fluxes, sometimes of doubtful value, is available in the patent literature.

The principle common to nearly all successful processes consists in refining the molten metal by stirring in an "inspissated" flux, which is also used later as a protective cover during superheating and pouring. Such an inspissated flux consists essentially of a chloride base, normally containing $MgCl_2$ and an alkali metal chloride to reduce its melting point, together with inspissating agents which increase the viscosity of the flux, either mechanically by remaining suspended in the protective base as inert solids, or by dissolving in the protective base and subsequently giving rise to a fine precipitate of an insoluble substance through chemical reaction. The most commonly used inspissating agents are CaF_2, MgF_2, and MgO. In the normal melting and refining process used by Magnesium Elektron, Limited, and its Associates, two fluxes * are employed: a fluid non-inspissated chloride flux, Melrasal *Z*, termed a protective flux, is used to protect the metal from oxidation during melting, and an inspissated flux, Melrasal *E*, is used subsequently for refining † the metal and as a protective cover during superheating and pouring. Before the invention of the inspissated flux, great difficulty was experienced in obtaining castings which were free from flux inclusions, and this inability to prepare clean metal held up the technical development of magnesium for many years.[1] Nowadays very little trouble with flux inclusions in commercial alloys is encountered, but a recent American paper [13] indicates the fluxing difficulties which may still arise in developing new alloys.

In speculating as to the manner in which the use of an inspissated flux enables flux-free metal to be obtained, it is usually assumed that

* For composition ranges see reference 28.

† In accordance with normal usage in the industry, the word "refining" will denote the removal of non-metallic impurities, e.g. oxide and flux: this process should not be confused with either grain refinement or chemical purification.

magnesium which has been melted contains suspended in it finely dispersed melting flux and MgO, together with dispersed chloride electrolyte in the case of virgin electrolytic metal,[1, 2, 6, 25] and that the essential function of the refining flux is in some way to remove the suspended impurities when it is stirred into the metal. The mechanisms which have been suggested are, broadly, that globules of inspissated flux are able to absorb the suspended oxide, thereby becoming sufficiently dense to settle readily, and are also able to thicken the suspended chloride inclusions so that these too settle out. It has also been suggested that the $MgCl_2$ in the flux is able to dissolve suspended MgO, or that the flux may coagulate a semi-colloidal suspension of MgO.[6]

Recently a good deal of work has been done on volatile refining and degassing agents. The use of anhydrous $FeCl_3$ for refining at Radenthein [7] was further developed during the war by I.G. Farbenindustrie under the name of " Elfinal " and its use was claimed to give improved mechanical properties, presumably due to degassing of the alloy.[8] Following the discovery of " carbon grain refinement " [9] as an alternative to the usual superheating process, gaseous or volatile fully chlorinated hydrocarbons have been employed to effect grain refinement and at the same time partial degassing of the metal.[10] Although it has been suggested that the use of these volatile substances, e.g. hexachlorethane, might eliminate the flux-refining process, it does not appear that they are being widely used for purposes other than degassing and grain refinement in conjunction with some type of flux refinement.

A long-term programme of research on fluxes was planned at the Clifton Junction Works of Magnesium Elektron, Limited, and begun early in 1942, one object of which was to elucidate the physical and chemical characteristics on which the refining action of an inspissated flux depends. For various reasons it was not possible to proceed systematically with the study of this subject, but by 1943 a good deal of fundamental ground had been covered in small *ad hoc* researches, leading to certain tentative conclusions concerning the behaviour and properties of fluxes which proved of great value in tackling the problem of inclusions in magnesium alloys containing zirconium. The present paper gives an account of these conclusions, modified where necessary by subsequent work, indicating the nature of the evidence on which they are based.

Section II deals with preliminary work on attempts to contaminate magnesium alloys with oxide and with flux, a study of experimental systems of transparent immiscible liquids whose physical properties appeared to resemble those of metal and flux, and with the application of calculations based on Stokes' law to the settling of chloride inclusions

under gravity. The effect of temperature on the settling of suspended oxide, and the mechanism of oxide removal by fluxes under certain conditions where settlement does not occur, are considered.

Section III deals with the origin of the flux inclusions which are occasionally found in cast metal. The functions and desirable properties of an inspissated flux are then discussed in Section IV, while Section V deals with the detection and examination of non-metallic inclusions in magnesium-base alloys. Conclusions are summarized in Section VI.

As the paper covers a relatively wide field, it has seemed best to transfer to an Appendix some of the evidence for certain conclusions, in order that the continuity of the paper should be less interfered with by experimental matter. It has also seemed best not to reserve a critical discussion of all the results until the end of the paper, and the discussion therefore proceeds subject by subject throughout the paper. Some general remarks on the work as a whole, however, follow the summarized conclusions in Section VI.

II.—Behaviour of Inclusions in a Body of Molten Metal.

1. *Preliminary Small-Scale Attempts to Prepare Contaminated Metal.*

For investigation of refining phenomena it seemed desirable to prepare, if possible, a uniform stock of contaminated metal which could be remelted and subjected to refining with various fluxes; the refined metal would then be cast and examined microscopically for oxide inclusions, and by exposure of sawn sections to steam for flux inclusions. (The substitution for steam of a controlled humidity of 80% was later found to give much greater sensitivity in flux detection—see Section V.)

The preliminary experiments described below were carried out on 5-lb. melts, approximately 3½ lb. of alloy being cast for examination in each case. Stirring, holding, and pouring of molten metal were in general performed at temperatures around 750° C.

Attempts were first made to disperse MgO in molten magnesium by applying MgO to the metal surface in the absence of flux, or allowing it to form *in situ* through burning, and vigorously stirring the melt for some minutes. On removing the excess MgO from the metal surface, covering with Melrasal *E* flux, and pouring into a simple die mould, no oxide was found in the cast metal. Even if the metal was poured immediately after stirring and without the surface being covered with *E* flux, very little oxide could be seen in the casting. After remelting this metal, covering with Melrasal *E*, and pouring without any stirring, no oxide could be detected in the cast metal.

Similar attempts were made to disperse protective flux (Melrasal *Z*)

and cell electrolyte in molten magnesium, the metal being die-cast into a slab mould $10 \times 10 \times 1\frac{1}{2}$ in., and the slab afterwards machined on each face and exposed to damp air. It was found that if the residual chlorides on the molten metal surface were absorbed with CaF_2 and removed, *E* flux applied, and the metal poured as soon as the flux had melted, the resulting metal showed no flux.

Where the metal was cast immediately after stirring, without any attempt being made to clean the metal surface, flux was present on the outside of the cast slab, but the interior appeared to be entirely flux-free. By stirring magnesium just above its melting point with the chlorides and pouring while still stirring into a cool mould so that solidification was rapid, metal containing a few large chloride inclusions was obtained. On remelting this metal without refining but pouring under a cover of Melrasal *E* flux, no trace of flux could be found in the resulting slab.

In other experiments, MgO mixed with small amounts of Melrasal *Z* was stirred into magnesium, but only by maintaining the stirring during pouring followed by rapid cooling could inclusions be trapped in the cast metal. These inclusions also disappeared when the metal was remelted.

From such preliminary experiments it appeared that stable suspensions of oxide or flux in molten magnesium were unlikely to be encountered under ordinary conditions; that inclusions of oxide and flux readily settled in molten metal; and therefore that inclusions found in cast metal probably arose either during or immediately before pouring.

2. *Study of Systems of Transparent Immiscible Liquids Resembling Metal and Flux.*

It was thought that the study of transparent immiscible liquids might throw light on the behaviour of flux and metal in the molten state, and in particular might give useful qualitative information concerning the effects of surface tension, viscosity, and density of the flux on the production and removal of flux inclusions. Particulars of the immiscible liquid systems studied are given in Appendix I (p. 468).

All the systems examined gave the same indications as to the behaviour of a protective flux layer on metal when disturbed. A considerable proportion of the "flux" sank through the "metal" in spherical globules which spread out on reaching the bottom and sides of the container. Some "flux" remained on the surface, particularly around the edges of the "metal" surface in contact with the container. The proportion of "flux" in the metal after a few minutes was negligible (see Fig. 1).

A rough attempt was made to calculate from these observations the approximate chloride content of unrefined metal cast from a 2-ton crucible 1 hr. after stirring-in 1% of protective flux. System *C* (Table IV, Appendix I) was used; 1% of the imitation protective flux was stirred in and the system allowed to stand for a time bearing the same ratio to 45 min.* as that of the depth of liquid in the beaker used to the

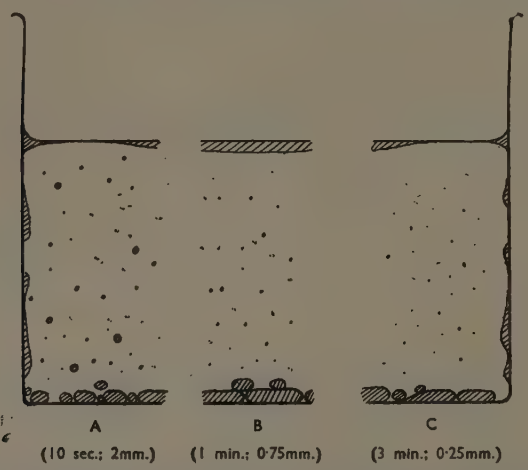

FIG. 1.—Experimental System of Immiscible Liquids Resembling Flux and Metal. Composite diagram illustrating appearance of System C, Table IV, at various times after stirring. (The times of settling and approximate diameter of the largest inclusions are given below each section of the diagram.)

metal depth in a 2-ton crucible. A rough estimation of the number of inclusions per centimetre cube was made, and their approximate size noted. The maximum size of inclusions present was also calculated from Stokes' law and was found to be in reasonable agreement with the visual estimation. From these data, the chloride content of metal in the case considered would be of the order of 0·00005%, less in fact than the lowest figure for the chloride content of refined metal from 2-ton crucibles which had been obtained by chemical analysis up to that time (0·0005%).†

* The normal time required for a 2-ton melt to cool from superheating to pouring temperature. (This work was carried out before the discovery of grain refinement at moderate temperatures by carbon inoculation.)

† The true chloride content of refined magnesium is too small to be determined chemically, being in all probability less than one-tenth of that introduced in dissolving a sample, even when using reagents of the highest purity.

The indications from experiments using immiscible liquids were, therefore, that chloride inclusions in a body of molten metal settled quickly, so that any such inclusions found in cast metal were unlikely to have arisen from chloride suspended in the body of the molten metal, whether or not any flux refining had been carried out.

3. *Application of Stokes' Law to the Settling Out of Flux Inclusions Under Gravity.*

In the possible event of fine globules of fluid (protective) flux becoming dispersed in a clean body of metal under special conditions, it appeared of interest to calculate approximately by Stokes' law what would be the order of size of the largest globules of flux remaining in suspension after the normal superheating and cooling process, and also to determine roughly the size of the corrosion spots to which such globules might give rise on exposure to damp air.

Calculations by Stokes' law (see Appendix II, p. 469) indicated that the order of size of the largest residual flux globules would be 0·05 mm. dia., corresponding to a chloride content of 0·05 γ. A rough indication of the size of the corrosion spots developing from such amounts of chloride on exposure to damp air may be obtained by placing a suitably sized droplet of a flux solution of known strength on a polished or machined magnesium surface, warming to evaporate the water, and exposing to damp air for a few days (see Section V. 2. (*b*)). In this way it appeared that, after normal foundry settling, corrosion spots developing from any residual suspended chloride would be under 0·5 mm. dia. Such very small corrosion spots could hardly be noticed unless specially looked for by exposure of a prepared surface of the metal in a humidity chamber, careful steps being taken to avoid access of dust (Appendix V, p. 476). Actually thin corrosion spots of this size, which are probably due to traces of chloride, are sometimes met with on normally refined standard alloys; they are usually associated with manganese-rich particles and are probably unconnected with the fluxes used. These inclusions do not appear to be of much practical consequence.

While the possibility of a fine dispersion of protective flux arising in clean metal appeared from the work already done to be remote, the indications of calculations by Stokes' law were, therefore, that under foundry settling conditions such a dispersion would not give rise to an unsatisfactory alloy, quite irrespective of whether or not any refining process was applied.

This conclusion is in accordance with foundry experience at the Clifton Junction Works, where it has been found that no trouble with flux inclusions results from omission of the " refining " process.

4. *Further Work on the Preparation of Contaminated Metal for Refining Tests.*

In order to test further the tentative conclusion indicated by the work described—namely that inclusions of oxide and flux do not remain suspended in molten metal but readily settle—various methods were tried for producing more effective dispersions of inclusions in magnesium, but without success being achieved. As this failure to produce suspensions of inclusions was so at variance with expectation, a record of the methods tried is given in Appendix III (p. 470).

The experiments (*a*) to (*h*) of Appendix III appear to show conclusively that clean metal can be poured from a badly contaminated melt without performing a refining operation, provided the metal surface is carefully cleaned and covered with a suitable inspissated flux and the melt allowed to stand for a short time before pouring.

More recently, in order to check the validity of this conclusion when using relatively short settling times and the improved humidity-chamber methods for flux detection which had since become available, three further experiments (*i*), (*j*), and (*k*) have been made with melts on a 40-lb. scale, in which every effort was made to contaminate the metal.

In the first experiment (*i*), the metal (miscellaneous scrap) was made to burn vigorously at 800° C. by stirring in damp MgO (4%) and 8% of cell electrolyte was added, some of which was vigorously plunged into the metal, the rest being left on the surface as a thick "sloppy" layer. Immediately stirring ceased, the fluid flux on the metal surface was absorbed with fluorspar and removed, Melrasal *E* applied, and the melt poured 5 min. later, i.e. less than 10 min. after ceasing the contaminating operations.

A second melt (experiment (*j*)) was contaminated by plunging the metal vigorously at 830° C. for 3 min., using just sufficient Melrasal *Z* to contaminate the skins produced. Immediately after ceasing the plunging, the metal surface was cleaned by covering with Melrasal *E*, removing the flux and absorbed oxide, and applying a fresh layer of flux. The metal was poured within 5 min. of ceasing the plunging, i.e. almost immediately after the fresh flux had melted.

In experiment (*k*) a melt of magnesium containing $4\frac{1}{2}\%$ zinc was poured into a second crucible containing 10% of a highly fluid fluoride mixture, the quaternary eutectic of LiF, CaF_2, MgF_2, and BaF_2, melting at 605° C. The objects of using the fluoride mixture were to provide a fluid mixture at the bottom of the melt and also to furnish a continuous supply of lithium and other electro-positive metals to offset the removal of these by $MgCl_2$ contained in the fluxes used, so as to maintain a melt

with greatly increased burning tendency. At about 800° C., the molten fluorides were brought up to the surface of the metal, stiffened with fluorspar, and plunged to the bottom of the pot, and the process continued until all the fluoride mixture had been thoroughly stiffened. This process took some 10 min. to perform and during this period very heavy burning and skinning of the metal occurred. Chloride fluxes were added in very small amounts to contaminate some of the oxide formed. When the stiffening process was complete, the metal surface was covered with Melrasal *E* flux, the crust of flux and oxide removed, fresh *E* flux applied, and the metal poured after holding for 10 min. at 800° C.

Even under the conditions of these last three melts—which were far more severe than are ever likely to occur in practice as regards the initial degree of contamination of the metal, the absence of refining, and the very short settling times involved—it was found that flux-free metal showing only negligible amounts of oxide was obtained.

It should perhaps be stressed that in these experiments very special care was taken in order to avoid flux inclusions arising from causes other than their presence in the body of the molten metal at the time of pouring. Such care was necessary since, from the nature of the melts, the risk of inclusions arising through known causes (see Section III) was in most cases greatly enhanced. In addition to the standard procedure already given,[3] the precautions described in Appendix III were applied to melts (*i*), (*j*), and (*k*), and also to many of the earlier melts.

5. *Successful Production of Metal Contaminated with Oxide (and Nitride) Inclusions of Limited Stability.*

Two ways were finally found of producing magnesium alloy contaminated with oxide which would remain in suspension on remelting in the absence of flux, provided the temperature did not exceed about 700° C.:

(*a*) Multiple remelting of the alloys in the absence of flux, the temperature being kept below about 700° C. at each remelt.

(*b*) Prolonged stirring of the alloys in the pasty state in the absence of flux, raising the temperature to about 700° C. and casting.

The oxide (and nitride) formed by the two methods is of different types, method (*a*) giving contamination mainly with skin, and method (*b*) contamination mainly with dispersed oxide (see Section V).

On remelting alloys produced by method (*a*) in the absence of flux, settling of the skins is found to occur to an increasing extent with rise in temperature (see Fig. 5, Plate XLIV); holding the alloy at 800° C. for, say, 5 min. will permit nearly complete settling of the skins, even on a very small scale (e.g. 1 or 2 kg.) where settling conditions are unfavour-

able. Covering the alloy with flux before pouring at temperatures of 760°–800° C. enables clean metal to be poured. Mere covering of the metal surface with flux at temperatures around 700° C. does not, however, permit clean metal to be poured (at least on a small scale), so that metal prepared by method (*a*) can be used for low-temperature refining experiments with flux.

In preparing contaminated metal by method (*b*), puddling is continued for 10 min. or longer, so that the layer of dispersed oxide which forms at the bottom of melts so puddled (see Appendix III, experiment (*a*)) is sufficiently deep to embrace the whole melt. On remelting such metal and raising the temperature above 700° C., some settling of the dispersed oxide occurs, resulting, unless the original dispersion was very dense, in the formation of a supernatant layer of clean metal which increases in depth as the temperature rises and the settled oxide packs more tightly. The rapidity of this settling is indicated by the marked segregation which can occur even in the short time required for an ingot to solidify (Fig. 18, Plate XLVIII). Removal of dispersed oxide by settling is more complete than that of skins, and the supernatant layer will contain only traces of dispersed oxide attached to manganese-rich particles or suspended skins.

The considerable increase in the ease of settling of suspended oxide present both in skin and in dispersed form, which occurs with rise in temperature, is no doubt due to the accompanying decrease in both the density and viscosity of the metal.

6. *Refining Experiments on Metal Contaminated with Skins and with Dispersed Oxide.*

In the following experiments on skin contamination, Elektron AM503 alloy, which had been remelted ten times in the absence of flux, was used, and the metal to be examined for oxide was cast into D.T.D. test-bars which were then fractured to show up any skin inclusions. Experiments were initially on a 2-kg. scale.

(1) The skin-contaminated alloy was melted in the absence of flux, heated to 720° C., covered with *E* flux, held 5 min., and poured; the cast metal showed considerable skin contamination.

(2) The alloy was melted in the absence of flux, heated to 720° C., stirred 1 min. with *E* flux, held 5 min., and poured; the cast metal was skin-free.

(3) The alloy was melted in a crucible previously coated with molten *E* flux and poured after holding 5 min. at 720° C. while dusting with sulphur to minimize oxidation; the cast metal showed considerable reduction in skin contamination compared with (1).

(4) The alloy was melted in an *E*-flux-coated pot and stirred for 1 min. at 720° C. using sulphur–boric acid mixture and held for 5 min.; the cast metal was skin-free.

(5) The alloy was melted without flux and transferred at 720° C. into a pot coated with molten *E* flux and held for 5 min. while dusting with sulphur–boric acid mixture; the cast metal was skin-free.

These experiments indicate that, under conditions where settling does not occur, suspended skins are readily removed from a body of molten metal by bringing the metal in contact with flux, which need not be stirred through the metal but may be present merely as a coating to the crucible. Experiment (3) suggests that even in the absence of any stirring of the melt sufficient circulation may occur, due to convection currents, &c., to cause removal of a considerable amount of suspended oxide; though an alternative explanation might be that the oxide settles, but, in the absence of flux to absorb and immobilize it, the oxide is disturbed by the currents produced when pouring and so enters the mould.

Further tests on the remelting of metal contaminated with skins or dispersed oxide in the absence of flux have been carried out on a larger scale (30–40 lb.), and it was found that, as in the small-scale tests, complete removal of suspended oxide did not occur on holding at temperatures up to 800° C., though oxide removal was generally satisfactory if the metal was covered with a layer of Melrasal *E*. Where the contaminated metal was melted under Melrasal *E* and also covered with the flux, oxide removal was complete.

The effect of using Melrasal *E* for melting is similar to that of coating a crucible with Melrasal *E*: e.g. if skin-contaminated metal is melted under flux, all flux removed from the metal surface and the melt stirred for 1 min. at 700° C. using sulphur, skin removal is readily effected.

Since it appears from Sub-Section 4. above that clean metal can always be obtained by remelting contaminated metal with flux and holding under a flux cover for a few minutes at, say, 800° C., while if the same metal is melted in the absence of flux and dusted with sulphur–boric acid mixture at 800° C. some few skins may remain in suspension, it is evident that in normal foundry practice removal of skins may not take place entirely by settling but may also occur through adherence of skins to flux coating the sides of the crucible.

Repetition of some of the experiments on metal which had been melted under sulphur and under sulphur–boric acid indicated that the presence of boric acid and sulphide in the skins did not affect their behaviour. Since boric acid can readily be estimated chemically in traces

(see Appendix V. 5.), use of sulphur–boric acid to minimize burning during preparation of skin-contaminated metal would enable a roughly quantitative comparison of the efficiency of refining of different fluxes to be made. Such work has not yet been attempted, but Table I indicates by this method the efficiency of Melrasal *E* in removing skins at 700° C.

TABLE I.—*Refining with Melrasal* E *of Metal Contaminated with Oxide–Boric Acid Skins.*

Sample.	Approx. Boron Content, %.
(*a*) Skin-contaminated Elektron AM503 produced by multiple remelting under sulphur containing 20% B_2O_3 . .	0·05
(*b*) Sample (*a*) remelted without flux, transferred into a pot coated with Melrasal *E* flux and stirred 1 min. under sulphur–boric acid	<0·001
(*c*) Sample (*a*) remelted without flux and transferred into a crucible coated with Melrasal *E*	0·005

TABLE II.—*Comparative Efficiencies of Skin Removal at 720° C. of Various Fluxes.*

Flux.				Test (1).	Test (2).
Ref.	Approx. Composition, wt.-%.		$MgCl_2$ Content.	Sides of Pot only Flux-Coated.	Flux also Applied to Metal Surface.
(1)	KCl–NaCl *	(55 : 45)	Nil	*B*–	*A*
(2)	$BaCl_2$–KCl–NaCl *	(50 : 30 : 20)	,,	*C*	*C*
(3)	$CaCl_2$–NaCl–KCl *	(50 : 30 : 20)	,,	*C*	*B*
(4)	$CaCl_2$–NaCl–KCl–$MgCl_2$ *	(40 : 30 : 20 : 10)	10	*B*	*A*
(5)	$BaCl_2$–$MgCl_2$–KCl *	(50 : 40 : 10)	40	*B*+	*A*
(6)	$MgCl_2$–$CaCl_2$–NaCl–KCl *	(40 : 25 : 20 : 15)	40	*B*+	*A*
(7)	Flux (6)–MgO †	(60 : 40)	24	*A*	*A*
(8)	,, (2)–MgF_2 †	(75 : 25)	Nil	*A*	*A*
(9)	,, (6)–CaF_2–MgO †	(70 : 20 : 10)	28	*A*	*A*
(10)	,, (5)–CaF_2 †	(75 : 25)	30	*A*	*A*

A = satisfactory skin removal.
B = partial skin removal.
C = little or no skin removal.

* Not inspissated.
† Inspissated to consistency of Melrasal *E*.

Some qualitative tests have, however, been attempted on the relative efficiencies of skin removal of several fluxes and standard chloride mixtures useful as flux constituents (Table II). Skin-contaminated Elektron AM503 alloy was melted without flux and transferred to a 1-kg.

crucible coated with the flux in question, and the melt was (test (1)) stirred for 1 min. while dusting with sulphur containing 10% boric acid, and (test (2)) stirred for 1 min. with the flux to be tested at 720° C. (In each case a small bar of the contaminated metal was poured at the time of transfer and fractured to ensure that the metal used in the tests was adequately contaminated with skins.)

These results appear to indicate that removal of suspended skins under conditions where settling does not occur is favoured by :

(*a*) Presence of inspissating agents in the flux.
(*b*) $MgCl_2$ content.

The beneficial effect of the inspissating agents may be accounted for partly by the greater thickness of the flux layer adhering to the pot walls and partly by the stickiness conferred on the chloride mixtures through the fluoride inspissating agents normally used.

Although it has sometimes been assumed that MgO is soluble in $MgCl_2$, the practical evidence to the contrary appears to be conclusive,[14] and the observed improvement in skin removal in the presence of $MgCl_2$ is probably due to the increased ease with which oxide is wetted by fluxes rich in $MgCl_2$. The effect of $MgCl_2$ in promoting wetting of MgO by flux at an MgO–air interface is referred to later.

7. *Attempts to Contaminate with Flux the Oxide Inclusions Produced Under Sub-Section* 5.

Having succeeded in producing oxide contamination which could persist on remelting below about 700° C., attempts were made to use this suspended oxide as a vehicle for traces of chloride so as to produce metal containing persistent chloride contamination for experiments in flux refinement at low temperatures.

Very light dustings of Melrasal *Z* flux were applied during production of contaminated metal by method (*a*) (Sub-Section 5.) above, but no persistent chloride inclusions were obtained.

It would be of interest to attempt to effect a still lighter chloride contamination of the suspended skins by intermittent application of chlorine during melting.

8. *Attempts to Refine Contaminated Metal by Use of Hexachlorethane.*

In view of the possibility that a degassing treatment with a volatile chloride might also remove suspended oxide, some experiments were made using hexachlorethane.

Magnesium alloys contaminated with skins or with oxide by the methods already described were melted and transferred at 720° C. into

clean crucibles. Refining was then carried out at 700°–720° C. by plunging from 0·1 to 2% of hexachlorethane below the metal surface in a suitable cradle. The metal surface was carefully cleaned and covered with *E* flux (see Appendix III) and the metal cast at 720° C. into test-bars, which were fractured to show up inclusions of skin or dispersed oxide (or nitride). Practically no indications of any removal of oxide by hexachlorethane were obtained, but complete removal of oxide occurred in all cases on subsequently stirring the melts for 1 min. under *E* flux at the same temperature (Fig. 7, Plate XLV).

It follows, however, from what has been said, that if contaminated metal is melted under a normal inspissated flux, degassed with hexachlorethane at, say, 720° C., covered with *E* flux and poured at normal temperatures (750°–800° C.), the resulting metal will be found to be oxide-free.

9. *Conclusions.*

From the experimental work described above some conclusions and inferences are possible.

(1) Inclusions of flux, with or without oxide and nitride, in a body of molten metal readily settle out on standing; there is no practical danger, with normal settling times, of flux inclusions arising in castings from protective flux suspended throughout the bulk of the molten metal, whether or not any flux-refining process is employed.

(2) (*a*) Inclusions of oxide (and nitride), whether in skin form or in dispersed form, in a body of molten metal settle out increasingly readily with rise in temperature.

Removal of skins by settling is fairly complete, and of dispersed oxide practically complete, after a few minutes' settling at temperatures above about 750° C.

(*b*) Oxide inclusions in either skin form or in dispersed form readily adhere to a suitable inspissated refining flux, present on the sides and bottom of the crucible, when brought into contact with it by convection currents or by stirring: very little stirring is required to effect complete removal of suspended oxide in this way.

(*c*) If a body of molten metal is covered by a layer of a suitable inspissated flux and held at temperatures above, say, 730° C. in a crucible coated with the flux, removal of suspended oxide from the body of the metal readily occurs by settling and by adherence to the flux layer: there is no practical danger, with normal settling times and temperatures, of oxide inclusions arising in castings from oxide suspended throughout the bulk of the molten metal, whether or not any flux-refining process is employed.

(3) The essential practical function of an inspissated refining flux is not, therefore, to remove suspended protective flux from the body of the metal, nor is it to remove suspended oxide inclusions on stirring the flux through the metal.

(4) Flux inclusions found in castings of standard alloys must accordingly arise from carelessness or improper procedure, provided, of course, that the quality of the flux used as a cover during pouring is satisfactory.

(5) The process of degassing magnesium alloys with hexachlorethane does not remove suspended oxide.

In view of the somewhat unexpected nature of these conclusions, a particular interest has been taken in all reports of flux inclusions in production work, in order to find out whether conditions can arise under which conclusion (1) is not valid. In all cases investigated, the inclusions were found to have resulted from either insufficient care in cleaning the metal surface before pouring, or from use of contaminated moulding sand and the presence of outcropping microporosity. Wherever the materials used were still available, the writer gave a practical demonstration that perfectly clean metal could be cast from the particular metal and flux used, even under more severe conditions than those actually employed (e.g. omitting superheating and reducing settling time).

III.—Origin of Flux Inclusions in Cast Metal.

As the result of a large body of experimental work and practical experience, it has become evident that flux inclusions in cast metal can arise in the following ways :

(1) Unabsorbed protective flux remaining on the metal surface, particularly round the edges of the pot.

(2) The presence of too fluid a flux cover, or insufficient care being taken in drawing back the flux cover from the lip of the pot before pouring.

(3) Leaving behind insufficient metal in the bottom of the pot at the end of pouring.

(4) Careless handling of the crucible in transferring from furnaces to pouring point; also jerking of the crucible back towards the vertical position after pouring each casting where several are poured from one melt.

(5) Presence of a brittle powdery flux cover due to excessively long heating of the metal. This may result in particles of dry powdery flux being carried over with the metal into the moulds.

(6) Failure to remove encrusted flux from the lip of the pot before pouring.

(7) Flux contamination of moulding sand used. This may give rise to contamination in areas where microporosity reaches to the surface.

The first four causes can all result in a thin film of flux passing into the mould, usually either along the sides or the under-side of the metal stream where it may not readily be seen. In die-casting with a very simple running system such a flux film is unlikely to break and, provided no burning of the metal stream occurs in pouring, the flux will merely be present as a superficial film on the casting which is readily removed on chromating. If the running system is more complicated or the stream turbulent, or if burning of the metal stream occurs during pouring, the external flux film may be broken, resulting in the presence of flux-contaminated skins in the casting (Figs. 13–14, Plate XLVII). The effect of a thin flux film on the pouring stream is well seen by using a stream of chlorine in place of sulphur to prevent burning, the chlorine producing a very thin $MgCl_2$ film on the metal.

The presence of small amounts of lithium, sodium, or barium in magnesium alloys promotes formation round the pouring stream of a thick irregular unstable oxide tube containing nitride, instead of the thin coherent oxide tube formed with the normal alloys which do not contain appreciable amounts of these elements.* Such oxide tubes containing nitride constantly break and are liable to carry traces of flux with them into the mould. In the presence of these electro-positive elements, therefore, it is necessary to use more powerful inhibitors than plain sulphur; for example, sulphur containing ammonium bi-fluoride or boric acid.

In practice much can be done to avoid breakage of the oxide tube by use of lip-axis pouring devices and suitable mould design so as to reduce the unsupported length of pouring stream to a minimum (Fig. 2).

Attention may be drawn to certain factors accentuating some of the causes of flux contamination listed. A flux cover which is abnormally fluid at the time of pouring may arise in the following ways :

(*a*) Abnormal initial fluidity of the inspissated flux itself.

(*b*) Presence of excessive amounts of *Z* flux on the metal surface before applying the *E* flux. (Excessive *Z* flux may be absorbed with *E* flux or fluorspar and removed.)

(*c*) Lifting the melt from the furnace after a shorter holding period than is normally used.

* Busk (U.S. Patent No. 2,385,685) states that lithium in amounts of 0·001–0·01% inhibits burning of magnesium. This is certainly not the case where the lithium content exceeds 0·01%; such amounts confer on magnesium a marked increase in tendency to burn. On the other hand, potassium, even in large amounts, confers no increase in tendency to burn on magnesium, probably on account of its extremely low solubility. In fact, as Busk remarks, potassium generally appears to inhibit inflammability.

(*d*) Omission of the superheating process where this is normally applied.

(*e*) Application of fresh flux to the metal surface shortly before pouring, e.g. to repair gaps in the flux cover caused by breakage on lifting the crucible from the furnace.

While with an abnormally fluid flux cover there is usually no difficulty in pouring clean metal using reasonable care, inclusions can result

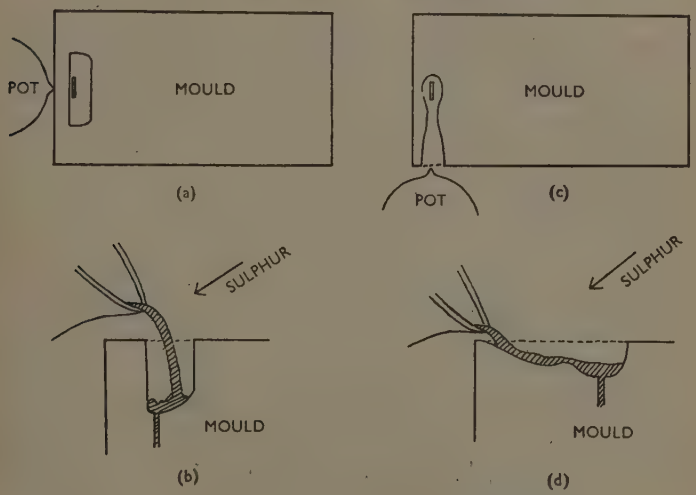

FIG. 2.—Pouring Arrangements for Sand Castings.

Method commonly adopted: (*a*) plan; (*b*) elevation.

Method involving much reduced risk of oxide skins in the casting: (*c*) plan; (*d*) elevation.

if the relatively " slap-dash " methods of cleaning the metal surface before pouring, which may safely be used with normal flux covers, are adopted.

If excessive fluid (non-inspissated) flux is used during melting and the molten metal is " washed " with fluid flux or with a mixture of fluid and inspissated fluxes, a good deal of fluid flux will collect at the bottom of the pot and the pot walls may become coated with it. In these circumstances, there is an increased risk of inclusions arising in the ways indicated under (3) and (4) above: jerking of the crucible may then even result in the appearance of a ring of fluid flux round the edge of the metal surface in contact with the crucible walls.

Contamination Arising from Flux in Moulding Sand.

Moulding sand which becomes accidentally contaminated with flux can act as a potential source of flux contamination in sand-cast alloys. This was first noticed in the course of experiments of the type already described, where molten metal was sand cast into narrow slabs for flux examination. In order to expose a large area of metal for flux examination, feeder heads on the slabs were dispensed with, complete soundness appearing unnecessary for the purpose. All such slabs on machining and exposure in the humidity chamber showed considerable areas of flux contamination (Fig. 8, Plate XLV), which were found to be associated with a peculiar form of microporosity, here termed " spider-microporosity " (Figs. 9–11, Plate XLVI). This type of microporosity consists of a system of micropores connected by fine dark lines. Further work showed that the flux contamination resulted from the presence of an external flux film on the metal which was sucked into microporous areas during solidification of the casting. Since no " spider-microporosity " contaminated with flux had been found in die-cast slabs poured from the same melts, it appeared probable that the external film on the molten metal had arisen from contact with the moulding sand used; and analysis showed the latter to contain 0·25% chloride corresponding to about 0·5% flux. In order to make sure that the flux film was not present on the metal entering the sand mould, unfed sand- and die-slabs were cast alternately from the same melt, and part of each die mould was maintained red hot with a welding torch during solidification of the casting, so as to form an area of outcropping microporosity into which any external flux film could be sucked. The die-cast slabs showed no flux contamination although extensive areas of outcropping microporosity were successfully formed; but all the sand slabs were contaminated with flux in the microporous regions. This showed that the included flux had resulted from contact with contaminated moulding sand.

Included flux arising from contaminated sand is apparently confined to alloys liable to show microporosity. None has been found in pure magnesium or the single-phase alloys Elektron AM503 (binary Mg–Mn) and ZA (binary Mg–Zr), and even with Elektron AZM alloy (Mg–6Al–1Zn) the contamination of castings is very largely superficial if they are adequately fed. Nevertheless, where conditions producing outcropping microporosity occur, quite small amounts of flux in sand, e.g. 0·1%, can give rise to this type of flux contamination, which can extend within a casting to a distance of about 1 in. from the surface. No doubt factors favouring microporosity, such as the inclusion in melts of corroded scrap, will promote the incidence of this type of contamination.

Origin of Oxide Inclusions in Castings.

The principal ways in which oxide inclusions can arise in castings have already been indicated in connection with the origin of flux inclusions, but for convenience a more complete statement of known causes of oxide inclusions is set out below.

(1) Breakage of oxide tube during pouring. This is promoted by the following factors :

(*a*) Insufficient care in cleaning the metal surface before pouring, leading to an oxide tube of irregular thickness.

(*b*) Application to the pouring stream of insufficient inhibitor or of an inhibitor unsuited to the alloy in question.

(*c*) Presence of elements in the alloy which promote nitride formation, e.g. sodium and barium.

(*d*) Failure to pour with the minimum height of unsupported pouring stream.

(*e*) Irregular pouring speed.

(2) Failure to keep downgates and gullies full of metal.

(3) Insufficient or unsuitable inhibitors for the alloy in question in the moulding sand. This will cause local burning at the surface of the casting with "spider-microporosity" in the underlying metal (see below).

(4) Unchecked burning of metal in risers and feeder heads followed by accidental jerking of the mould before solidification is complete.

(5) Insufficient care being taken to re-clean the metal surface in the pot before refilling up any large feeder heads directly from the pot.

(6) Presence of damp mould dressing on metallic chills, launders, &c.

If much burning has been allowed to occur during melting and the quantity of flux added has been very inadequate, a good deal of oxide unabsorbed by flux may be present near the bottom of the melt or loosely attached to the crucible sides, and this may give rise to oxide inclusions in the following ways :

(7) Leaving insufficient metal behind in the crucible after pouring.

(8) Lack of care in handling the crucible during pouring.

Inclusions produced in this way are unlikely to be free from flux and therefore come under the category of flux inclusions. Even if melting has been very badly carried out, subsequent stirring of the melt with the inspissated flux, if properly performed, will absorb and immobilize loose oxide near the bottom and sides of the crucible (see later) and prevent inclusions arising as in (8).

IV.—Functions and Desirable Properties of an Inspissated Flux.

1. *Functions of an Inspissated Flux and of the Refining Process.*

From consideration of the behaviour of inclusions in molten metal and the origin of inclusions found in cast metal, some conclusions and speculations about the essential functions and desirable properties of an inspissated flux are possible.

Since the use of a suitable inspissated flux merely as a cover during pouring the melt enables flux-free metal to be cast, almost without regard to the previous history of the melt, the capacity to form a flux cover of suitable properties is clearly the most important function of an inspissated flux. Without the use of an inspissated flux cover or alternatively of solid inspissated agents, it is a matter of some difficulty to pour flux-free metal because of the presence of unabsorbed fluid protective flux on the metal surface, particularly round the edges in contact with the pot walls. In these circumstances, it is not surprising that before the invention of inspissated fluxes much flux-contaminated metal was produced; and the source of the contamination, as has previously been stated, was erroneously attributed to flux disseminated throughout the molten metal before pouring.

When the use of an inspissated flux for refining and covering the metal was found to eliminate this flux contamination, it appears to have been assumed that the disseminated protective flux was removed by the inspissated flux during the refining process, thus leading to some rather improbable suggestions as to the mechanism by which this occurred, and to a belief that it is necessary for the inspissated flux to be stirred completely through the molten metal for proper refining.

Having absorbed and therefore immobilized protective flux on the metal surface and provided a protective cover of suitable properties, thus enabling clean metal to be poured, a second important duty of an inspissated flux is clearly to minimize to the greatest possible extent the risk of flux inclusions arising in the other ways indicated in the previous Section. And this minimizing of the risk of flux inclusions due to various causes appears to be the function of the "refining" process most important in practice.

In the refining process, metal covered with an inspissated flux layer is vigorously stirred, using a rotary motion, either for a given time, say, 1 min., or until no flux remains on the metal surface. During stirring, the flux becomes distributed on the sides and bottom of the crucible and some may remain on the metal surface. Several pheno-

mena tending to reduce the risk of flux inclusions arising from the causes already listed (Section III) occur during refining.

(1) The rotation of the metal brings to the surface any excess fluid flux coating the sides of the crucible slightly below the metal level, so that such flux is rendered harmless either by absorption into the original inspissated flux cover during stirring, or by subsequent application of fresh inspissated flux to the metal surface when stirring has ceased. This reduces the risk of flux inclusions arising in the ways (1) and (2) of Section III. The formation of a central vortex in the metal during stirring assists this process by encouraging an upward movement of the metal in contact with the walls of the pot.

(2) The inspissated flux stirred to the sides and bottom of the crucible is able to absorb and immobilize to some extent excessive protective flux already there, thus reducing the risk of inclusions arising in the ways (3) and (4) of Section III.

(3) If melting has been inefficiently conducted, the stirring brings to the metal surface, in the form of glowing embers, oxide loosely adhering to the crucible walls, while oxide at the bottom of the melt tends to be absorbed and immobilized by the flux stirred through the metal. These phenomena reduce the risk of inclusions arising particularly in way (3) of Section III.

A further phenomenon occurring during the refining process is the adherence of any residual suspended oxide to flux present on the sides of the crucible as already indicated (Section II. 6.).

Before considering in greater detail what are the properties of an inspissated flux which will enable it to perform the functions described, an interesting general inference is possible. Since the functions of the inspissated flux appear to be mainly physical in nature, it is likely that the chemical constitution of the flux will be of no great importance provided the constituents are chemically inert to magnesium and can give rise to suitable physical properties. This inference has now been thoroughly borne out: no single chemical constituent is necessary for the production of a satisfactory inspissated flux; for example, fluxes have been made in which $MgCl_2$, CaF_2, and MgO are separately absent, and, indeed, in the absence of either fluorides or oxides (see Table III).

Nevertheless, in designing fluxes from given constituents or for special purposes, there are important chemical aspects which require consideration. Some of those dealing with the attainment of desirable physical properties are mentioned below, but questions involving the introduction and removal of trace elements will not be discussed in this paper.

The desirable properties of an inspissated flux are now considered

TABLE III.—*Chemical Composition of Various Inspissated Refining Fluxes Giving Flux-Free Metal.*

Ref. No.	Protective Base.					Inspissating Agents.							General Type.	Special Remarks.
	$MgCl_2$, wt.-%.	$CaCl_2$, wt.-%.	NaCl, wt.-%.	KCl, wt.-%.	$BaCl_2$, wt.-%.	BaF_2, wt.-%.	MgF_2, wt.-%.	CaF_2, wt.-%.	MgO, wt.-%.	"R_2O_3", wt.-%.	SiO_2, wt.-%.	C, wt.-%.		
1	...	41	26	9	...	...	24	...	...	...	...	...	$MgCl_2$-free.	$CaCl_2$-rich.
2	...	19	11	7·5	37·5	...	25	...	...	...	...	...		$BaCl_2$-rich.
3	...	...	17	26	40	...	17	...	...	...	...	...		$CaCl_2$-free.
4	65	...	...	...	...	...	35	...	...	...	...	...	No alkali metal chlorides.	
5	20	18	11	7	...	...	...	...	16	8	20	0·2	Fluoride-free.	
6	38	...	...	31	...	...	31	...	...	...	...	...	Oxide-free (see also fluxes 1 to 5).	KCl-rich.
7	29	20	12	6	...	...	...	33	...	...	...	...		Ba-free.
8	27	...	...	8	35	24	...	...	...	...	...	...		Ba-rich.
9	31	7	6	25	...	...	...	21	5	...	...	...	Standard inspissated fluxes.	Elrasal *D*.*
10	34	15	10	7	...	...	...	21	13	...	...	...		Melrasal *E*.
11	50	...	...	20	...	...	...	15	15	...	...	...		Dow 310.

* Contains 5% H_2O in the form of hydrated carnallite.

Note : The fluxes numbered 1, 2, 3, 5, 7, 8, and 10 in Table III are protected by patents or patent applications.[17]

and some indications are given later under Sub-Section 3. of this Section of the ways in which they can be achieved.

2. *Desirable Properties of an Inspissated Flux.*

Those properties of a suitable flux cover for use in pouring are dealt with first :

(a) *Consistency on Application.*

The flux cover must be coherent and of such a consistency shortly after application that it can be drawn back before pouring without leaving a perceptible film or loose particles on the exposed metal surface ; and when drawn back, it must more or less " stay put ". These conditions permit of a fairly wide latitude of consistency, but other considerations, mentioned later, limit this latitude considerably.

(b) *Homogeneity.*

The cover should not separate into a drier layer above, and a thin fluid layer below (" liquation effect "), nor form a dry powdery layer on the top (" dry-top effect ").

(c) *Ability to Absorb Oxide.*

The inspissated flux is normally applied to melts as soon as melting is complete. At this stage pools of protective flux and some MgO may be present on the metal surface and, unless excessive in amount, these are not usually removed before application of inspissated flux. An inspissated flux must therefore be able to absorb considerable amounts of oxide without itself becoming too dry.

(d) *Ability to Absorb Protective Flux.*

The flux must also be able to absorb considerable amounts of fluid protective flux without itself becoming too fluid. Requirements (c) and (d) therefore limit the permissible latitude in consistency.

(e) *Embrittlement on Standing.*

The flux cover should not become brittle, powdery, or unduly hard during reasonable periods of superheating or holding in the furnace.

(f) *Insensitivity to Temperature.*

The flux cover should be of approximately the optimum consistency when applied to metal at any temperature from the liquidus of the protective base up to, say, 950° C.

(g) *Absence of " Non-Wetting " Tendencies.*

The flux should not develop " non-wetting " tendencies at high temperatures. Some types of flux will form on metal a cover of satis-

factory appearance, but when this cover is disturbed the flux will rapidly withdraw to the sides of the pot leaving a large area of metal exposed to oxidation. This is termed the " non-wetting " effect.

(h) *Spreading Power.*

When freshly applied it is desirable that the flux on melting should tend to spread out slightly so as to cover the whole surface. A tendency of the flux to collect into isolated pools on melting is not, however, of much consequence, apart from increasing the quantity required to cover the metal, provided that the cover does not show non-wetting tendencies once melting is complete.

Two other properties not connected with the behaviour of the flux when molten may also be mentioned :

(i) " *Shakeability* ".

The flux should be capable of being readily shaken on to the metal surface as a fine powder. This is a function of the physical state of the constituents as well as of the conditions of storage.

(j) *Hygroscopicity.*

This should be as low as possible, since hygroscopicity is not in itself desirable and can lead to various complications.

An inspissated flux which is to be used for refining as well as covering should have the following properties :

(k) " *Stirrability* ".

The flux should be capable of being at least partly stirred through the metal.

(l) *Stickiness.*

The flux should adhere readily to the sides and bottom of the crucible.

In addition, the need for properties (c) and (d) in a flux which is to be used for refining as well as covering is accentuated in order that functions (2) and (3) of Section IV. 1. can be properly performed without the flux becoming too fluid or too dry to be capable of being stirred through the metal or to give a cover of suitable consistency.

Considering all these properties, it will be noticed that those bearing on the question of optimum consistency fall into two groups with opposed requirements :

The flux must be relatively dry on application :

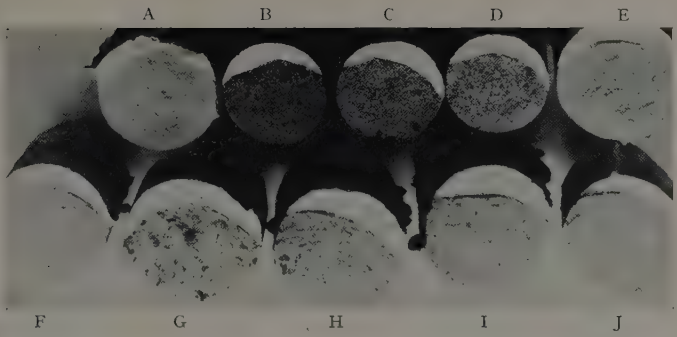

FIG. 5.—Effect of Temperature on the Settling of Skins and Dispersed Oxide.

A–E. Settling of dispersed oxide in Elektron A8.

B, C, D. Fractured bars cast after settling for 5 min. at 720°, 760°, 800° C., respectively.

A, E. The same metal as B after stirring for 1 min. with Melrasal *E* flux.

F–J. Settling of skin inclusions in Elektron AM503.

G, H, I. Fractured bars cast after settling for 5 min. at 720°, 760°, 800° C., respectively.

F, J. The same metal as G after stirring for 1 min. with Melrasal *E* flux.

FIG. 6.—Polished Ingot Section of Elektron A8 Contaminated with Oxide Inclusions Made by Stirring the Alloy Below the Liquidus Temperature in the Absence of Flux. × 1½.

[*To face p.* 454.

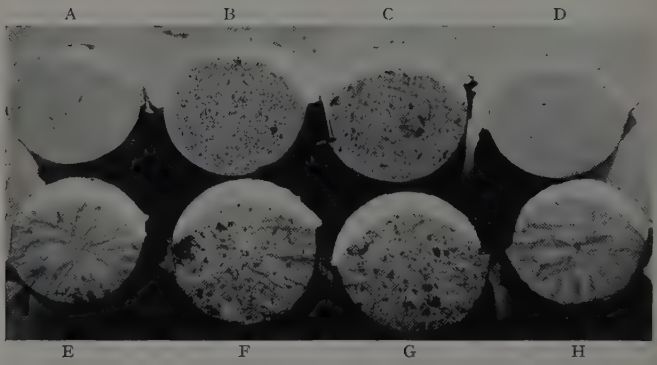

FIG. 7.—Effect of Hexachlorethane Degassing Treatment on Suspended Oxide.

B. Elektron A8 contaminated with dispersed oxide.
C. The same metal treated with hexachlorethane.
A, D. The same metal subsequently stirred for 1 min. with Melrasal *E*.
F. Elektron AM503 contaminated with skin inclusions.
G. The same metal treated with hexachlorethane.
E, H. The same metal subsequently stirred for 1 min. with Melrasal *E*.

(Some small shadows on *E* and *H* should not be confused with skin inclusions, which were entirely absent from these specimens.)

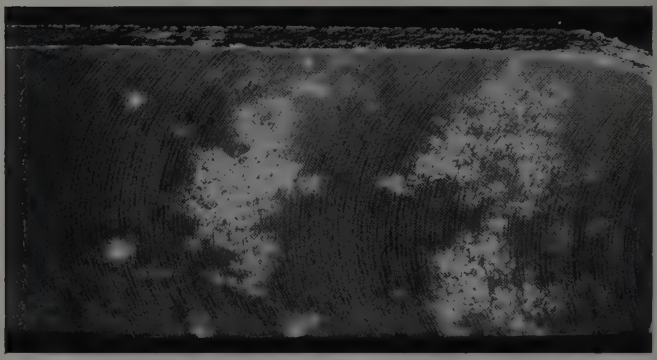

FIG. 8.—Corrosion in Sand-Cast Elektron A8 Slab Due to Flux-Contaminated Microporosity; Resulting from Outcropping Microporosity Caused by Poor Feeding and the Presence of 0·25% Flux in the Moulding Sand Used. Oblique illumination.

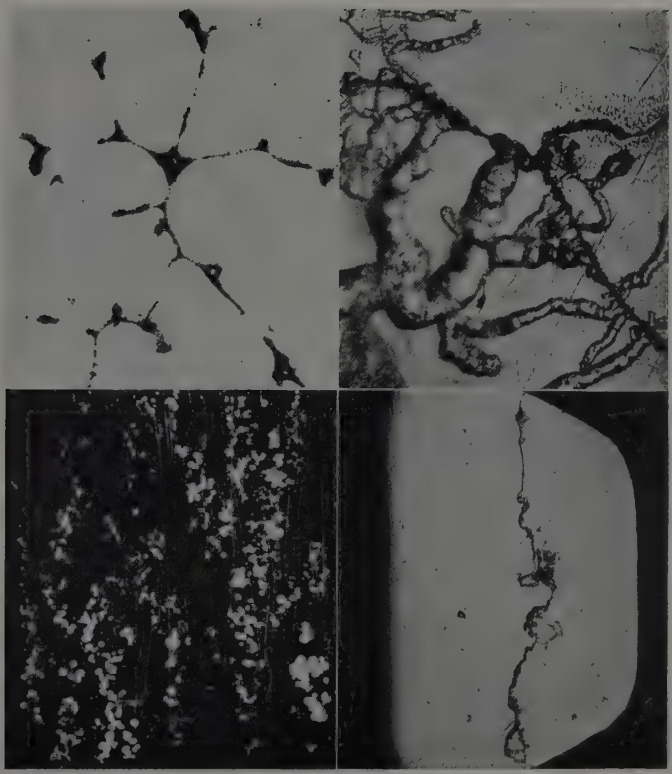

FIG. 9.—Typical Appearance of "Spider Microporosity" Contaminated with Flux in Magnesium–3% Zinc Alloy. × 200.

FIG. 10.—Development of Corrosion in Magnesium–4½% Zinc Alloy Caused by Traces of Flux Associated with the "Threads" of "Spider Microporosity". × 1000.

FIG. 11.—Typical Striated Appearance in Fine-Grained Alloy (Magnesium–Zinc–Zirconium) of Corrosion Due to Flux-Contaminated Microporosity. Oblique illumination. × 7.

FIG. 12.—Section Through a Casting Skin Trapped in the Feeder Head of a Die-Bar. × 1.

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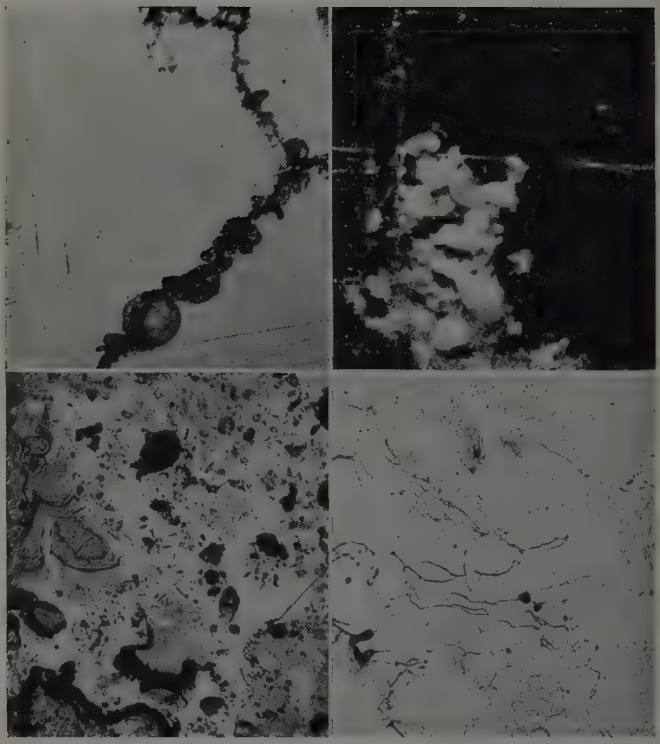

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FIG. 13.—Oxide Skin Contaminated with Flux. × 500.
FIG. 14.—Typical Appearance of Corrosion Developing from Flux-Contaminated Skins. Oblique illumination. × 15.
FIG. 15.—Layer of Suspended Oxide in Elektron A8 Stirred without Flux Below Liquidus Temperature. × 20.
FIG. 16.—Very Fine Casting Skin Barely Visible before Etching (2% nital). ×250.

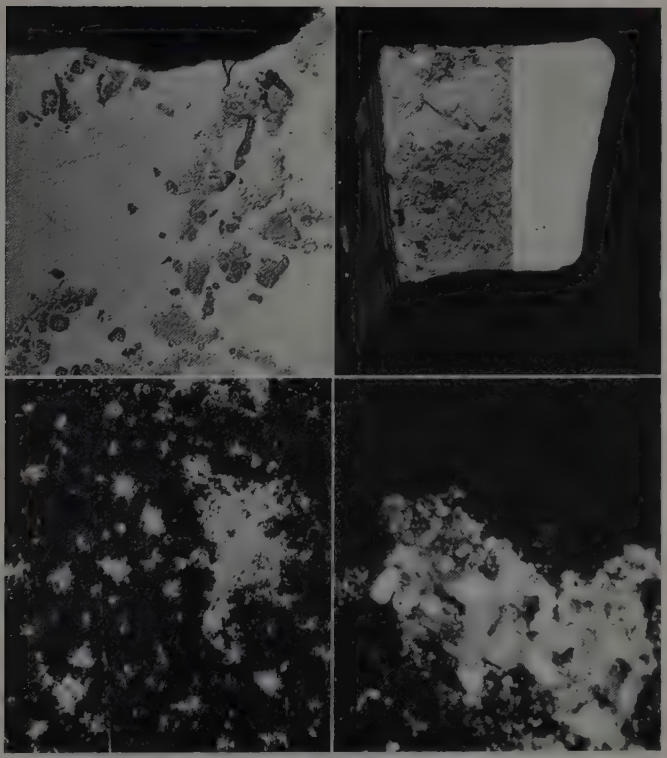

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FIG. 17.—Strings of Dislodged "Dotted Phase" Trapped by Solidification while Sinking through the Melt. × 20.

FIG. 18.—Fracture of Ingot Cast at 750° C. from Metal Similar to Fig. 5 (G). Note the rapid settling of the oxide which has occurred.

FIG. 19.—Corrosion not Due to Flux: flux-like corrosion due to access of chloride-contaminated dust to surface of flux-free magnesium on exposure to air indoors for 48 hr. Oblique illumination. × 20.

FIG. 20.—Corrosion Spot Developing in Elektron AM503 from Manganese-Rich Particles Contaminated with Chloride. Oblique illumination. × 30.

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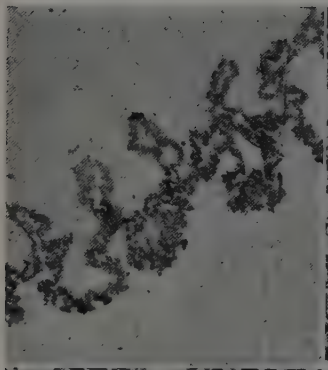

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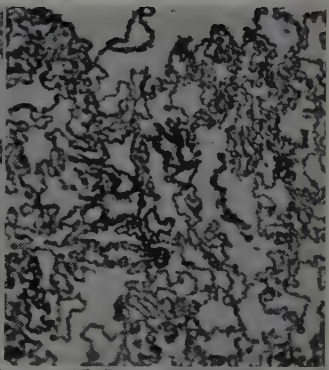

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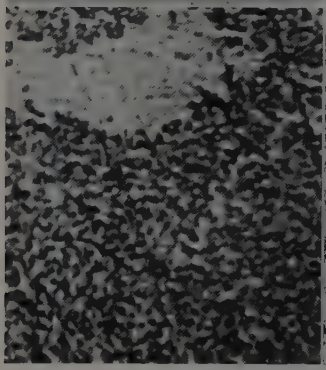

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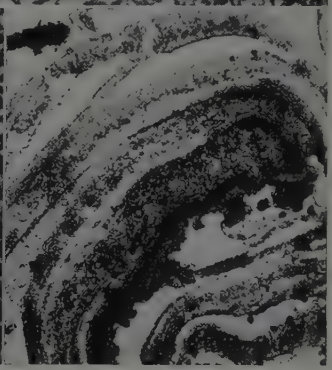

FIG. 21.—Tangled Chains of " Dotted Phase ". × 600.
FIG. 22.—Tangled Chains of " Dotted Phase ". × 500.
FIG. 23.—Structure of " Dotted Phase " in Elektron A8. × 2000.
FIG. 24.—Massive " Dotted Phase ". × 350.

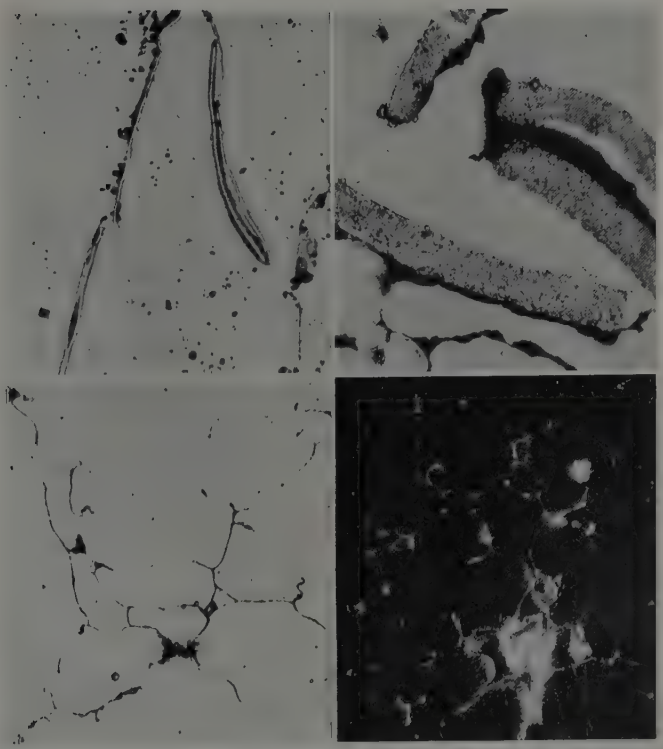

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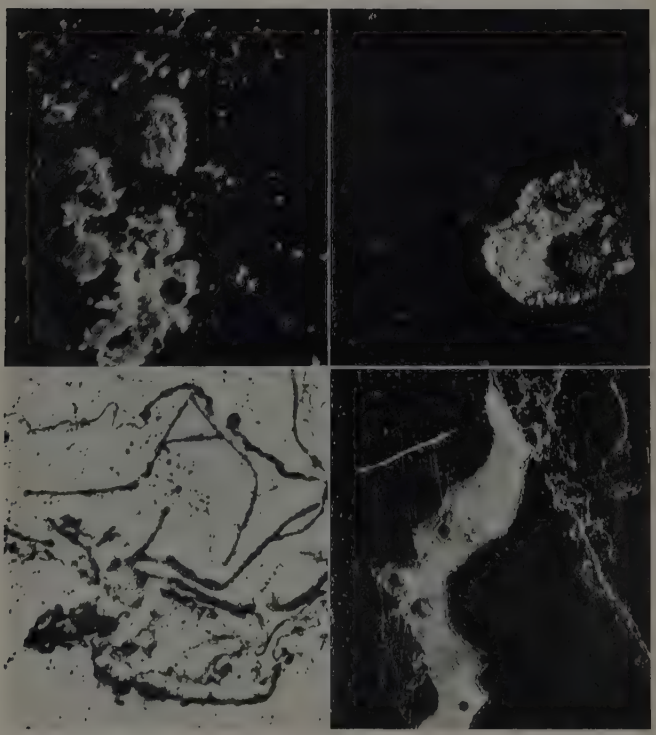
FIG. 25.—Strips of Massive "Dotted Phase" Formed in Metal Adjacent to a Skin. × 60.

FIG. 26.—Same as Fig. 25. × 600.

FIG. 27.—Flux-Free "Spider Microporosity" in AZ91, Associated with a Casting Skin (not shown in field). × 500.

FIG. 28.—"Spider Microporosity" Associated with Boric Acid, Showing Deliquescence of Boric Acid after a Short Exposure to Damp Air. Oblique illumination. × 25.



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31 32

FIG. 29.—"Spider Microporosity" Associated with Nitride, Showing Efflorescence Due to Decomposition of Nitride to Oxide. Oblique illumination. × 25.

FIG. 30.—Massive Nitride Inclusion Formed by Stirring Elektron A8 under Nitrogen. Oblique illumination. × 60.

FIG. 31.—Thick Sulphide-Rich Skins in Elektron AM503 Formed by Casting Burning Metal under SO_2. × 45.

FIG. 32.—Massive Sulphide Inclusion in Elektron AM503 Stirred under SO_2. Oblique illumination. × 45.

(a) to provide a cover of proper consistency to permit pouring shortly after application, and

(d) for good absorptive power for fluid flux.

The flux must be relatively fluid on application :

(c) for good ability to absorb oxide, and

(e) to provide a cover of suitable consistency after superheating.

Therefore, if a single inspissated flux is used for both refining and covering during pouring, it is evident that the consistency on application must represent a compromise between those ideally suited for the performance of functions (a) and (d) on the one hand and (c) and (e) on the other.

(m) *Permissible Latitude in Composition.*

An inspissated flux should therefore possess considerable permissible latitude in composition, i.e. the consistency should change very little with large additions of MgO or protective flux.

Flux systems vary greatly in respect of this property and whereas it may be possible to produce a flux of suitable consistency as a cover for use in pouring from almost any low-melting inert chloride protective base and inert inspissating agents (subject to conditions dealt with later), it is not always easy to arrange for the flux to possess a sufficiently wide latitude in composition for satisfactory commercial production and use. In flux systems where the permissible latitude is large, " all-purpose " fluxes, which are satisfactory for melting, refining, and covering during superheating and pouring, are possible.

(n) *Density.*

The question of the density of the molten flux relative to that of the metal is not normally a matter of much importance, since practically any inspissated flux will automatically have a sufficiently high density relative to that of the alloys being considered to permit rapid settling of inclusions. In the case of the non-inspissated fluxes, however, this is not always the case and a well known American brand of protective flux, based on the low-melting compound $2KCl.MgCl_2$, incorporates a small amount of $BaCl_2$ to correct for the low density of the former.

3. *Production of Some Desirable Properties in Inspissated Fluxes.*

In the present paper, only the properties of (a) consistency, (b) homogeneity, (f) temperature insensitivity, and (g) freedom from non-wetting tendencies, which prove to be inter-related, will be considered; consideration of the other physical properties would lead beyond its scope.

As already indicated, the consistency of the flux must lie within a fairly narrow range representing a compromise between the satisfaction of opposing requirements. There are several possible ways of inspissating a protective base to give a flux of suitable consistency, e.g. :

(i) Addition of an insoluble, infusible, inert constituent to stiffen the chloride mixture mechanically.

(ii) Addition of a soluble substance which will dissolve in a protective base and either increase its viscosity or react with some constituent of the protective base to produce a fine precipitate of an insoluble substance.

For convenient distinction, these two processes may be termed " stiffening " and " thickening " processes respectively, and included in the general term " inspissating ".

To obtain some insight into the nature of these processes, it may be of interest to consider briefly the inspissation of a fluid protective base of low $MgCl_2$ content separately with MgO and with CaF_2; these latter substances behave as stiffening and thickening agents, respectively. A typical example of such a base is the protective flux Melrasal *MZ*,[18] consisting roughly of $CaCl_2$, NaCl, KCl, and $MgCl_2$ in the approximate weight ratios of 4 : 3 : 2 : 1.

(a) *Properties of Fluxes Made by Inspissating Melrasal* MZ *with MgO.*

The upper part of the flux cover can be pushed back to reveal a thin fluid layer underneath in contact with the metal (" liquation effect "). The two layers may be separated by an air space formed by a tendency of the crust to arch-up in places (" pie-crust effect "). There is a tendency for small bubbles to form in the crust, which is therefore of low density and relatively difficult to stir through the metal. After drying off during superheating, the resulting porous crust tends to crumble when disturbed.

The flux tends to be slow in melting and to appear slightly dry and powdery on top owing to a reluctance of the protective base to wet the MgO particles there (" dry-top effect "). This lack of homogeneity in the flux cover is fairly typical of fluxes inspissated with inert insoluble stiffening agents and, whereas the undesirable effects can often be reduced or eliminated in various ways—for example, by pre-fusing the stiffening agents into the protective base—such fluxes have usually a narrow latitude in composition and are not satisfactory.

The presence of MgO does not appreciably affect the tendency of the protective base to wet the metal, and if a gap is made in the flux cover the flux tends to flow inwards so as to close it. By incorporation of sufficient MgO, actual flow of the flux may, of course, be prevented.

The quantity of MgO required to give a flux of proper consistency is independent of the temperature between 650° and 950° C.

(b) *Properties of Fluxes Made by Inspissating Melrasal* MZ *with* CaF_2.

If the same chloride mixture is inspissated with CaF_2, it is found that, while the "liquation" and "pie-crust" effects are substantially absent, the quantity of CaF_2 required to give the proper consistency increases rapidly with temperature; a flux which appears satisfactory at 700° C. becomes hopelessly fluid and strongly non-wetting at 850°–900° C. If such a flux cover is then disturbed, the flux flows outwards towards the sides of the pot, thus exposing a large area of metal to oxidation.

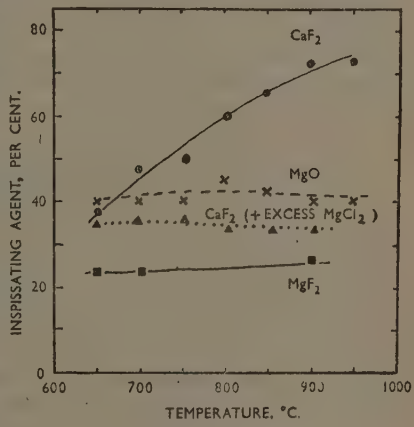

Fig. 3.—Effect of Temperature on the Proportions of Inspissating Agents Required to Inspissate the Protective Base Melrasal *MZ* ($CaCl_2$ 40, NaCl 30, KCl 20, $MgCl_2$ 10%) to Standard Refining Consistency.

The increase with temperature in the quantity of CaF_2 required to give a flux of good consistency is due to increasing solubility of the CaF_2 with temperature; and the presence of dissolved fluoride in the protective base is associated with increase in the contact angle between flux and metal, which gives an "oily" appearance to the flux and non-wetting tendencies.

If, however, $MgCl_2$ is present in a protective base in sufficient amounts, inspissation with CaF_2 is found to give rise to none of these difficulties (Fig. 3); the flux covers obtained are homogeneous and the permissible latitude is considerable. This indicates either (*a*) that CaF_2 tends to be insoluble in $MgCl_2$-rich chloride mixtures at all temperatures; or (*b*) that CaF_2 dissolves readily in such chloride mixtures, MgF_2 being precipitated, and that the MgF_2 is practically insoluble at all temperatures. (The formation of MgF_2 from CaF_2 and $MgCl_2$ is referred to in the literature.[15])

Since the quantity of MgF_2 required to inspissate the *MZ* protective base is found to be independent of temperature and non-wetting effects

do not arise, explanation (*b*) appears likely and has been verified by microscopic, X-ray, and analytical methods, the latter being specially devised to avoid interchange of radicals during analysis (see Appendix IV, p. 473).

From the above considerations and from experience with fluxes of widely different compositions, some general conclusions concerning the relation between chemical composition and desirable physical properties have been reached.

It is normally desirable that some fluoride should be present in inspissated fluxes in order to avoid the lack of homogeneity resulting from inspissation with purely inert stiffening agents. And in order to confer temperature-insensitivity and to avoid non-wetting tendencies, a stoichiometric excess of $MgCl_2$ over the fluorides present is required.*

V.—The Detection and Examination of Non-Metallic Inclusions in Magnesium-Base Alloys.

Having dealt in the preceding Sections with the behaviour and origin of inclusions and the nature and function of the inspissated refining flux, methods for the detection and examination of inclusions are now considered. The actual experimental details of the methods used are for the most part given in Appendix V (p. 476).

For convenience the inclusions may be considered under the head of "corrosive" and "non-corrosive" inclusions.

1. "*Non-Corrosive*" *Inclusions.*

Non-corrosive inclusions, which include oxide, nitride, sulphide, and boric acid derivatives, are dealt with first for convenience, because some types can become contaminated with flux, thereby giving rise to corrosive inclusions.

Two non-destructive methods are available for detection of the larger inclusions, namely, radiography and supersonic inspection. Although MgO is radiographically denser than magnesium, oxide skins are frequently associated with voids in the metal and therefore appear dark on the negative radiograph. Since most magnesium alloys contain manganese, some of which is present as a suspension of insoluble particles, it not infrequently happens that oxide skins sweep up and entrap sufficient of the radiographically dense manganese-rich particles to appear light instead of dark on the radiograph. Dispersed oxide, free from associated voids, appears light on the radiograph. A considerable

* For reasons given later (Appendix IV), any MgF_2 incorporated in the flux may be excluded in calculating the $MgCl_2$ requirement.

amount of experience, based on destructive examination, is required to interpret correctly the radiographic, and also supersonic, indications.

Destructive detection of non-corrosive inclusions may be made by microscopic examination of polished sections, radiography of thin sections, and examination of fractured surfaces. If polished or machined surfaces are exposed to damp air, as described later for flux detection, the presence of skins may sometimes be indicated by corrosion due to traces of associated flux; boric acid inclusions so exposed will develop a practically non-corrosive moist efflorescence, and nitride inclusions a non-corrosive dry efflorescence. Sensitive chemical tests for boric acid and nitride are given later (see Appendix V). Radiography applied to thin sections cut from castings is naturally much more sensitive for detecting inclusions than when applied to whole castings. Skins present at fractured surfaces are readily visible to the naked eye as black or brownish inclusions; and the examination of fractured surfaces, as is well known, provides a convenient, rapid, and sensitive method of detecting their presence.

Microscopic examination indicates the occurrence of several types of structure among the non-metallic non-corrosive inclusions which may be present, the principal types being " skins ", " dotted phase ", " dispersed oxide " and " spider-microporosity ". These types of structures were obtained during the earlier work on the controlled production of casting skins of various types and of dispersed oxide (Appendix III), so that their nature and origin are fairly clear.

(a) " *Skins* ".

When perfectly clean magnesium is poured under sulphur at low temperature, the casting skins appear as very fine dark lines (Fig. 16, Plate XLVII), frequently tangled, but if the metal surface is slightly oxidized thicker dark lines are present (Fig. 26, Plate L). These dark lines, which are evidently voids between two surfaces of magnesium lined with a film or films, are the parts of casting-skin structures which may show flux contamination and no doubt represent the remains of a metal–air interface. Unless manganese-rich particles have been swept up in some quantity, these fine skins will not usually appear on radiographs of ½-in. thick slabs of metal.

The presence in cast metal of this type of skin may be taken to indicate breakage of the oxide tube in pouring or else oxidation of the metal stream in the running system.

(b) " *Dotted Phase* ".

If visible burning occurs during pouring, the casting skins show a brownish " dotted phase " (Fig. 23, Plate XLIX), which may be present

in tangled chains (Figs. 21–22, Plate XLIX) or in striated massive form (Fig. 24, Plate XLIX), or which may occur in massive strips on one or both sides of the dark line indicating an original interface (Figs. 25–26, Plate L). This dotted phase is apparently not continuous oxide but a fine compact suspension in magnesium; it is formed in the body of the metal but adjacent to an interface. When visible burning occurs on the feeder head of a casting which has not yet solidified, or when merely visible "oxidation" occurs if sodium, lithium, or barium are present,* a thick layer of "dotted phase" forms in the body of the metal in contact with the surface skin. This layer has little coherence, and if the mould is tapped the layer breaks up, strings of "dotted phase" sinking through the metal until stopped by solidification (see Fig. 17, Plate XLVIII). These skins are frequently directly visible on ¼-in.-thick radiograph sections.

The presence of "dotted phase", with or without a skin interface, indicates that burning of the metal, as opposed to mere oxidation, has occurred in the pouring stream or running system.

(c) "*Dispersed Oxide*".

This is present in quantity at the bottom of melts which have been stirred in the pasty state and appears to consist of broken-up strings of "dotted phase" (Fig. 15, Plate XLVII). X-ray powder photographs of a dense dispersion from the bottom of an Elektron A8 alloy melt failed to give any patterns other than those due to the magnesium and aluminium, and it appears necessary to concentrate further the dispersed oxide, e.g. by centrifuging the molten alloy, before its precise nature can be determined.

(d) "*Spider-Microporosity*".

Another structure obtained in the production of casting skins trapped in test-bars when using alloys in which microporosity can occur was "spider-microporosity". The occurrence of spider-microporosity contaminated with flux, resulting from a superficial chloride film being sucked into an area of outcropping microporosity during solidification, has already been mentioned (p. 448). The spider-microporosity associated with the casting skins trapped in test-bars (Appendix III (*g*)) was frequently flux-free (see Fig. 27, Plate L) and present in the metal below the casting skin, in cases where some burning of the first portion of metal poured into the mould had occurred and this metal had been allowed to become practically solid before pouring in

* Since the "dotted phase" does not appear to contain nitride, it is remarkable that its formation should be promoted by lithium and barium which are known to promote nitride formation.

the next portion of metal. It may presumably, therefore, be formed through air being sucked into outcropping microporosity, and the "threads" of the spider-microporosity would then be attributable to oxide films.

Further work has shown that other substances capable of forming films can be sucked into outcropping microporosity to produce spider-microporosity, and examples of spider-microporosity have been produced in which the "threads" consist mainly of sulphide, nitride, and boric acid derivatives (Fig. 28, Plate L). Nitride spider-microporosity can arise during the heat-treatment of castings containing outcropping microporosity (Fig. 29, Plate LI).

The presence of spider-microporosity in a casting therefore indicates outcropping porosity into which air or other film-forming substance has been sucked; and the remedies are to eliminate the porosity by degassing the melt and applying better feeding to the casting, or to prevent the porosity from reaching to the surface by suitable application of chills.

(e) *Nitride Inclusions.*

Examination with Nessler's solution (see Appendix V. 6.) of the casting skins obtained above showed that nitride, where present, was associated with the interface films and not with the "dotted phase" in the metal. Stirring of magnesium alloys under nitrogen to exclude oxide formation gave nitride distributed in roughly spherical inclusions (Fig. 30, Plate LI): no strings or fine dispersions of nitride were obtained.

(f) *Sulphide Inclusions.*

Stirring of magnesium alloys at temperatures over about 750° C. under SO_2 to exclude nitride formation gives rise to sulphide-rich inclusions in the form of thick skins (Fig. 31, Plate LI) or in hard massive form (Fig. 32, Plate LI). These inclusions are quite different from ordinary oxide inclusions which may frequently contain a little sulphide.

2. *Corrosive Inclusions.*

These include all types of chloride-containing inclusions. Such inclusions alone are not detectable by radiographic or supersonic examination, though these methods will indicate certain structures, such as oxide skins, oxide or clusters of particles with which flux may possibly be associated.

(a) *Detection of Corrosive Inclusions by Exposure of a Prepared Surface to Damp Air.*

In the early work, as already mentioned, metal to be examined for flux was sectioned and exposed to steam for some time. This process

caused much discoloration of the metal surface, making the detection of minor inclusions a difficult matter. Sawn surfaces were also tested with CrO_3 solution. With a view to following the growth of inclusions microscopically, a number of magnesium alloy sections were given a micro-polish and exposed to damp air. The micro-polished surface was found to constitute a very sensitive test for traces of flux. Dust present in the air caused development of numerous white corrosion spots after one or two days' exposure indoors (see Fig. 19, Plate XLVIII), and it was therefore necessary to exclude dust by exposing the specimen to damp air in a closed chamber. Mr. C. J. Bushrod suggested that the humidity should be maintained slightly below that at which pure magnesium is said to corrode in air by introducing into the chamber a saturated aqueous solution of a suitable salt. "Hypo" was eventually adopted, since this salt will absorb traces of chlorine present in the air in addition to providing a suitable humidity (relative humidity 80% at room temperature). A suitable time of exposure was found to be 48 hr.

This method for "developing" any chloride-containing inclusions present at a metal surface is still in use, but in most cases it is more convenient to examine a finely machined rather than a polished surface. The substitution of machining for polishing as a method for preparation of specimens for flux testing requires special precautions which are described later.

(b) *Chemical and Spectroscopic Examination of Corrosion Spots.*

In view of the observed production of flux-like corrosion spots by dust, probably contaminated with chlorides, and the possibility of the occurrence of corrosion spots through causes quite unconnected with chlorides, it was clearly necessary to establish chemical or other methods for determining the nature and origin of corrosion spots developing in the humidity chamber.

(i) *Testing for Chloride.*—Direct application of $AgNO_3$ solution to corrosion spots on magnesium was not practicable owing to blackening of the metal surface by precipitated silver. Attempts to dissolve $AgNO_3$ in organic solvents which might inhibit the reaction with magnesium but permit that with chloride, were unsuccessful. A test with $AgNO_3$, involving removal of the corrosion product from the metal and capable of detecting 1 γ of chloride in a corrosion spot and of roughly estimating larger amounts, was subsequently developed (see Appendix V). This test was checked against "artificial" corrosion spots produced by placing known amounts of chloride on a polished magnesium surface and exposing in the humidity chamber. The chloride was added either as a minute solid crystal or as a droplet of a dilute aqueous solu-

tion, the dimensions of the crystal or droplet being measured under the microscope and the quantity of chloride calculated. In this way the amounts of chloride required to produce corrosion spots of various sizes were obtained. Spots of 3–4 mm. dia. after exposure in the humidity chamber for 48 hr., for example, were found to be caused by amounts of flux of the order of 30 γ.

From a comparison of the amounts of chloride actually found in corrosion spots with the amounts required to produce artificial corrosion spots of the same size, it was evident that the corrosion spots greater than about 0·75 mm. dia. which appeared on polished metal surfaces after standard exposure in the humidity chamber, were caused by traces of chloride, as was expected. The very small corrosion spots of the order of 0·3 mm. dia. and less, which may appear fairly frequently on standard alloys and are probably of little consequence from any point of view, also seem to be due to traces of chloride which, however, must only be of the order of 0·1 γ chloride per spot. This conclusion is based on microscopic observations on the effects of CrO_3 solution on the spots and on synthetic corrosion spots produced from evaporated droplets of dilute chloride solutions.

The use of CrO_3 solution in detecting chlorides in conjunction with the microscope has been studied. This reagent, which can be applied directly to the magnesium surface, is more sensitive to chloride than $AgNO_3$, but less selective, a weak positive reaction being obtained in the presence of nitrate and sulphate.

Estimations of the iron contents of corrosion spots were made in a few instances, but it did not appear that iron particles played an appreciable part in the development of corrosion spots in the humidity chamber. On the other hand, gross corrosion spots developing outside the humidity chamber on flux-free metal, resulting from accidental superficial contamination, were frequently rich in iron and in places brownish in appearance to the eye. The presence in a corrosion spot of much iron is a clear indication that it is of external origin and not due to flux in the metal. (For details of test, see Appendix V.)

(ii) *Testing for Calcium.*—To assist in distinguishing between chloride corrosion spots which were caused by inclusions of Melrasal fluxes and those produced by accidental superficial contamination, a sensitive method for detection of calcium in corrosion spots was desirable. (Calcium is present in the standard Melrasal *E* flux, but not usually in superficial contamination.) Chemical and spectroscopic methods for examination were tried, and it was found possible to detect about 10 γ calcium chemically and 40 γ spectroscopically (see Appendix V). The latter method of examination is, of course, quicker and more convenient, and

with suitable refinements could be made to detect smaller amounts of calcium.

(c) *Microscopic Examination of Corrosion Spots.*

Microscopic examination of corrosion spots will usually indicate their origin, and this has proved of particular value in alloys other than the standard alloys, where special types of inclusions may be present. The actual technique of microscopic examination is dealt with in Appendix V.

In the standard alloys, the following types of flux inclusions can occur:

Type I.—Roughly spherical holes filled with flux.

Type II.—Flux associated with oxide (or nitride) skins without "dotted phase".

Type III.—Flux associated with massive oxide (or nitride) "dotted phase".

Type IV.—Flux associated with microporosity, generally of the "spider" type.

Type V.—Chloride associated with manganese-rich particles.

In addition, corrosion spots due to accidental superficial contamination may be present.

Type-I inclusions, which are simply inclusions of flux unassociated with any other structure, are of very rare occurrence, and apparently can only arise if the flux cover is rather fluid and is pushed back from the lip or under the metal surface very carelessly *immediately* before pouring.

Type-II inclusions are relatively of more frequent occurrence and can arise in any of the ways (1) to (5) of Section III, but most usually in ways (1) and (2).

Type-III inclusions indicate that burning of the metal as opposed to gentle oxidation has occurred at some stage during pouring, or, alternatively, the presence of certain nitride-promoting electro-positive metals, e.g. barium, in the alloy.

Type-IV inclusions in a casting indicate the presence of an external film of chloride on the metal during solidification, which must have arisen either from chlorides in the moulding sand, or in ways (1) to (4) of Section III and in particular (2) and (3). In addition, the feeding system of the casting may have been unsatisfactory or, alternatively, the melt may have shown abnormal tendency towards microporosity, probably on account of the presence of hydrogen.

Chloride inclusions associated with manganese-rich particles are sometimes met with in standard alloys (in particular in the Mg 1·5% Mn alloy), where manganese has been incorporated by means of $MnCl_2$.

They are unconnected with the fluxes used and represent a borderline case of a phenomenon which is discussed in detail, in a further paper [26] dealing with magnesium-base alloys containing zirconium. Generally, chloride inclusions associated with manganese-rich particles are very minute, giving corrosion spots up to about 0·5 mm. dia. under standard exposure in the humidity chamber, and their presence constitutes no practical problem in standard alloys. A large specimen of such an inclusion, which was obtained from the bottom of a small scale magnesium–manganese alloy melt where a very large excess of $MnCl_2$ had been used and the melt was allowed to solidify in the crucible, is shown in Fig. 20 (Plate XLVIII).

Corrosion due to accidental superficial contamination, arising either from contact with a chloride-contaminated surface or through access of contaminated dust, will frequently show iron scale or non-deliquescent dust particles under the microscope, and on removal of the corrosion product the underlying metal will be sound and will not give rise to further corrosion on exposure in the humidity chamber.

VI.—Summary of Conclusions.

The main conclusions reached in this paper are set out below, those already formulated in the text being repeated here for convenience.

1. *Behaviour of Inclusions in Molten Metal.*

(*a*) Inclusions of flux with or without oxide or nitride in a body of molten metal readily settle out on standing.

(*b*) There is no practical danger with normal settling times of flux inclusions arising in castings from protective flux suspended throughout the bulk of molten metal, whether or not any flux-refining process is employed.

(*c*) Inclusions of oxide (and nitride), whether in skin form or in dispersed form, in a body of molten metal settle out increasingly readily with increase in temperature.

Removal of skins by settling is fairly complete and of dispersed oxide practically complete after a few minutes' settling at temperatures above about 750° C.

(*d*) Oxide inclusions in either skin form or in dispersed form readily adhere to a suitable inspissated flux present on the sides and the bottom of the crucible when brought into contact with it by convection currents or by stirring.

(*e*) If a body of molten metal is covered by a layer of a suitable inspissated flux and held at temperatures above about 730° C. in a crucible

coated with the flux, removal of suspended oxide from the body of the metal readily occurs by settling and by adherence to the flux layer.

(*f*) There is no practical danger with normal settling times and temperatures of oxide inclusions arising in castings from oxide suspended throughout the bulk of the molten metal, whether or not any flux-refining process is employed.

(*g*) The degassing of magnesium alloys with hexachlorethane does not remove suspended oxide.

2. *Origin of Flux Inclusions Found in Castings.*

(*a*) Flux inclusions can arise in castings in numerous ways which may be grouped as follows:

(i) The flux cover is in an unsatisfactory physical state.

(ii) Insufficient care is taken in observing certain precautions to ensure a clean metal stream.

(iii) The moulding sand is contaminated with flux or other chlorides, and outcropping microporosity is present in the casting.

(*b*) Inclusions arising in any of these ways do not persist on remelting.

3. *Origin of Oxide Inclusions Found in Castings.*

Oxide inclusions may arise in castings in various ways which may be summarized as follows:

(*a*) Breakage of the oxide tube during pouring.

(*b*) Failure to keep downgates and gulleys full of metal.

(*c*) Insufficient or unsuitable inhibitors in the moulding sand.

(*d*) Direct filling up of feeder heads from the crucible.

(*e*) Unchecked burning of metal in risers and feeder heads.

(*f*) Damp mould dressing on chills, launders, &c.

(*g*) Excessive burning of the metal and use of insufficient flux in melting, coupled with lack of care in pouring.

4. *Functions of an Inspissated Flux.*

(*a*) The essential function of an inspissated flux is not to remove suspended impurities from the metal during the refining process.

(*b*) The essential function of an inspissated flux is to provide a cover on the metal of suitable physical properties to enable a clean stream of metal to be poured.

(*c*) The effect of stirring the melt with an inspissated flux is to reduce the risk of flux inclusions arising under abnormal conditions or through careless procedure. (The risk of oxide inclusions resulting from inefficient melting and lack of care in pouring is also reduced.)

(*d*) The chemical nature of the inspissated flux is of secondary importance provided the constituents are inert to magnesium and can give rise to a flux cover of suitable physical properties.

5. *Relation Between Chemical Constituents of an Inspissated Flux and Development of Desirable Physical Properties.*

(*a*) The presence of a fluoride or pre-fusion of the flux is desirable to achieve homogeneity of the flux cover.

(*b*) The $MgCl_2$ content should be at least stoichiometrically equivalent to the fluorides (other than MgF_2) present, so as to avoid temperature sensitivity and non-wetting effects.

VII.—Deductions.

Considering these conclusions very briefly, the most important result is probably the discordance between the experimental facts and the traditional views on the origin of inclusions and the function of a refining flux which are set out in the Introduction to the paper, and which have been widely accepted in the industry. Some suggested reasons for the origin of the traditional views have already been mentioned.

A practical conclusion of some importance follows: whereas on the older view, if oxide or flux inclusions were found in castings the fault was ascribed to the inefficiency of the flux used or to improper carrying out of the flux-refining procedure, it is now quite evident that the fault will almost certainly lie either in the pouring operation, and particularly in the prior cleaning of the metal surface, or in the use of contaminated moulding sand under conditions producing outcropping microporosity. The methods given for examination of inclusions should enable the precise types of inclusion and their origin to be determined, so that suitable preventive steps can be taken to avoid their recurrence.

The formation of inclusions in magnesium alloys by the sucking of film-forming substances into areas of outcropping microporosity during solidification of castings is an interesting phenomenon which does not appear to have been previously reported.

Acknowledgements.

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APPENDIX I.

Systems of Transparent Immiscible Liquids Resembling Metal and Flux.

On account of the high surface tensions of molten metals, it seemed very unlikely that a system of two immiscible liquids could be found in which the surface tensions, viscosities, and densities of the two phases should be simultaneously equal to those of protective flux and metal. It was therefore necessary to consider what were the more important factors on which the production and stability of inclusions depended and to arrange for these factors to be as similar as possible in the two systems.

As a first approximation, it was considered desirable that the ratio of the surface tensions, viscosities, and densities of the two phases should be the same in each system, i.e.

$$\frac{\gamma_1}{\gamma_2} = \frac{\gamma_f}{\gamma_m}; \quad \frac{\eta_1}{\eta_2} = \frac{\eta_f}{\eta_m}; \quad \frac{\rho_1}{\rho_2} = \frac{\rho_f}{\rho_m}$$

where γ, η, and ρ represent surface tensions, viscosities, and densities, respectively, and the suffixes 1, 2, f, and m refer to the two phases of the experimental system, protective flux, and metal, respectively. It was necessary that the upper phase should spread to some extent on the lower and that it should wet the containing vessel, whereas the lower phase should not. In systems where the upper phase was organic and the lower aqueous, this latter condition was achieved by lightly greasing the sides of the glass beaker used. It was also desirable that the rates of settling of the same-sized inclusions of one phase in the other should be the same in both systems. Assuming spherical inclusions, this condition requires, by Stokes' law, that

$$\frac{\rho_1 - \rho_2}{\eta_2} = \frac{\rho_f - \rho_m}{\eta_m}.$$

Some uncertainty existed when this work was done as to the numerical values of the physical properties of flux and metal in the molten states. The rough figures first assumed are given in Table IV, System *A*, and System *C* represents an attempt to simulate these conditions with two organic liquids. It was later found that the

Table IV.—*Particulars of Some Experimental Systems Resembling Protective Flux and Metal.*

System.	Phases.	Properties.			Ratios of Properties, &c.				
		η, poises.	γ, dynes/cm.	ρ, g./c.c.	η_1/η_2.	γ_1/γ_2.	ρ_1/ρ_2.	$\frac{\rho_1 - \rho_2}{\eta_2}$	$\frac{\gamma_2 - \gamma_1}{\eta_1 + \eta_2}$
A	Protective flux I. Metal.	0·013 * 0·02 *	100 * 550	1·65 1·5	0·6	0·2	1·1	8	14,000
B	Protective flux II. Metal.	0·015 * 0·013 †	140 * 550	1·65 1·5	1·2	0·3	1·1	11	15,000
C	40% Chloroform : 60% toluene (by vol.). H_2O.	0·006 0·010	27 73	1·08 1·00	0·6	0·4	1·1	11	290
D	60% water-glass : 40% H_2O (by vol.) + 1 g. sodium oleate/100 c.c. 5% chloroform : 95% aniline (by vol.).	0·048 0·037	39 43	1·21 1·05	1·3	0·9	1·2	5	47

* Inferred from published data on analogous substances.
† Calculated by Andrade's method.[11]

viscosity of magnesium at the melting point could be approximately calculated from Andrade's theory of liquid viscosity,[11] and the calculated figure appears in the data for System *B* (magnesium with a different protective flux). The best over-all approximation to this latter system obtained with transparent immiscible liquids is shown as System *D*. The "flux" phases in the experimental Systems *C* and *D* were tinted with Monolite Red and eosin respectively to show up the inclusions. It will be seen from Table IV that the systems investigated appear to represent quite a fair degree of approximation to magnesium and protective flux.

Later, it was thought desirable to consider some function which would give an indication of the tendency of a flux cover to break up into spherical inclusions on stirring. It was assumed that this tendency depended, among other things, on the extent to which the interfacial tension could overcome the work against viscous forces necessary to break off the inclusion and might be represented qualitatively by $\frac{\gamma_2 - \gamma_1}{\eta_1 + \eta_2}$ (see Table IV). Refining fluxes would have a corresponding value of about unity or less. Since the addition of "stiffening agents" (p. 456) could scarcely alter the interfacial tension between metal and flux, it would be expected that the tendency of a stiffened flux crust to break up into small inclusions on stirring would decrease with increasing viscosity.

Preliminary attempts made to reproduce refining phenomena using glycerine and water-glass as refining fluxes showed some promise, but the work was abandoned when it became evident that the absorption of suspended inclusions of protective flux is not a principal function of an inspissated flux during the refining process.

APPENDIX II.

Application of Stokes' Law to the Settling of Chloride Inclusions Under Gravity.

Stokes' law deals with the terminal velocity reached by a spherical body settling under gravity in a stationary viscous medium.

Let V cm./sec. = terminal velocity of body.
$(D - d)$ g./c.c. = difference in density between body and medium.
r cm. = radius of body.
η C.G.S. units = coeff. of viscosity of the medium,

then Stokes' law can be expressed as

$$r^2 = \frac{9\eta V}{2g(D - d)}.$$

Neglecting convection, the settling of droplets of cell electrolyte in a 2-ton crucible may be considered. The height of the metal may be taken as 150 cm., and the settling time as 2500 sec. Inclusions which do not settle out must, therefore, have a terminal velocity less than $\frac{150}{2500}$ cm./sec. = 0·06 cm./sec. Taking $D - d$ for cell electrolyte as 0·25 and η for magnesium as 0·013 (see Table IV), this limiting terminal velocity corresponds to a droplet of 0·005 cm. dia., 0·1 γ in weight, and containing 0·05 γ chloride.

A similar figure is obtained if a 300-lb. crucible settling for 30 min. is considered.

This chloride content is of the same order as that required to produce the very small corrosion spots (0·3 mm. dia.) such as may occur fairly frequently on standard alloys and appear to be of no consequence from any point of view.

It is probable that, under foundry conditions, settling of suspended droplets of flux, if present, would be considerably interfered with by convection currents and that effective settling would mainly occur after the pot had been removed from the furnace. Effective settling periods of approximately 10 min. and 5 min. for a 2-ton and a 300-lb. crucible, respectively, appear, however, to be amply sufficient to prevent the occurrence of corrosion spots of the smallest size which could be regarded as of some consequence, say, 1 mm. dia. (see p. 463).

APPENDIX III.

Methods Tried for Producing Suspensions of Inclusions in Molten Metal.

In the following attempts to produce suspensions of inclusions in molten metal, each melt involved 10 lb. of metal of which about 7 lb. was poured off for examination, unless otherwise stated.

(*a*) Elektron A8 alloy was melted in a clean crucible without flux and stirred in the pasty state, i.e. at a temperature considerably below its liquidus, for 3 min., during which time no flux was applied and the oxide formed became uniformly dispersed in the pasty metal (Fig. 6, Plate XLIV).

On merely remelting this paste, covering with *E* flux, holding for 10 min. at 750°–800° C., and then pouring, no oxide was found in the bulk of the cast metal. The same result was obtained when sodium and lithium were added to the pasty alloy in small amounts to promote burning. A loosely packed layer of dispersed oxide was present in the metal at the bottom of the melt. (See Fig. 15, Plate XLVII.)

(*b*) Method (*a*) was repeated with the addition of flux in very small amounts, sufficient being used to contaminate the oxide skins without absorbing them. The pasty metal was remelted, covered with *E* flux, held for 10 min. at 750°–800° C. as before, and then poured. No trace of flux was found in the cast metal.

(*c*) ZnO was stirred into pasty Elektron A8 alloy in amounts up to 10% with a view to forming a dispersion of MgO in the alloy by chemical reaction. On treating this paste in the same way as before, no oxide could be seen microscopically in the cast metal. Static mechanical properties of test-bars cast from a melt treated similarly were normal. (Analysis of the metal for zinc confirmed that the ZnO had been reduced and MgO therefore formed.)

(*d*) Since a fine dispersion of MgO in metal might not be readily detectable microscopically, method (*c*) was repeated using ZnO, the particles of which had been previously coated with a very thin layer of Melrasal *Z* flux, so that the presence of included MgO in the remelted pasty alloy might be indicated by traces of associated flux. Small amounts of the fluorides of sodium, lithium, and barium were added to promote burning of the alloy in the pasty state. In this experiment also clean metal was obtained. (The approximate contents of the electro-positive elements present in the final alloy were as follows: Li 0·08, Na 0·1, Ba 0·06%.)

(*e*) Melrasal *Z* flux was uniformly dispersed in Elektron A8 alloy in the pasty state in amounts up to 10%, but no flux was detectable in the alloys obtained on remelting and casting.

(*f*) Method (*e*) was repeated using pure magnesium and a fluid flux of approximately the same density as the metal. This flux was prepared by adjusting the composition of a molten bath of $MgCl_2$ and KCl at 800° C. until globules of magnesium floated completely immersed in the flux. A dispersion of 10% of the flux in Elektron A8 was prepared, remelted, and poured under Melrasal *E*. Very surprisingly, the cast metal showed no flux inclusions: presumably this was due to different rates of change of density of the metal and flux with temperature, sufficient density difference having existed at some temperature between the melting point of the metal and 800° C. to enable the inclusions to settle out.

(*g*) It was thought that "casting skins", on account of their larger surface area, would tend to settle out less readily in molten metal than the more massive oxide and nitride present as broken-down films or in particulate form in previous experiments, and that such casting skins might therefore act as a vehicle for the production of stable flux inclusions in metal, i.e. inclusions which would not disappear on remelting without stirring or refining. Metal contaminated with casting skins was prepared by pouring the metal into a vertical chill mould in small amounts, allowing the cast metal to become just solid or pasty between additions. In this way a test-bar containing half-a-dozen casting skins was obtained, which could be sectioned longitudinally, so enabling the skins to be examined microscopically (Fig. 12, Plate XLVI). By varying the pouring temperature, allowing the metal to burn before pouring, or applying sulphur, other inhibitors or traces

of flux, as desired, bars of metal each containing skins of a particular type were obtained for remelting and refining tests.

No inclusions were, however, found in metal obtained by remelting bars containing casting skins with Melrasal *E* and pouring, without refining, under a cover of Melrasal *E* flux.

(*h*) In view of statements in the literature and a belief in the industry that magnesium remelted more than two or three times without refining shows oxide contamination; some magnesium was melted under Melrasal *E* flux on a 5-lb. scale and poured under Melrasal *E* flux, and the process repeated 16 times without applying any stirring operation. Care was taken at all stages to avoid agitating the metal. The metal was finally cast into a narrow slab which was machined and exposed in the humidity chamber for flux and later examined microscopically and radiographically for oxide. Neither flux nor oxide was found. A similar result was obtained on repeating the experiment with Elektron AM503 alloy on a larger scale (40 lb.) and remelting 10 times.

Note on Practical Precautions Taken in Pouring Experimental Melts Treated with Contaminating Agents.

In cleaning the metal surface of oxide or fluid flux, the appropriate cleaning agent, i.e. Melrasal *E* flux or fluorspar, was applied in sufficient amounts to produce a viscous paste on the metal, and Melrasal *E* was dusted very lightly on the metal surface during removal of the paste with a spoon in order to prevent oxidation of the metal from occurring. Where necessary, this process was repeated. Before applying the final cover of Melrasal *E*, the inside of the pot on the pouring side and the lip were carefully scraped to remove scale and encrusted flux down to the metal level. Using a small spade-shaped spoon, the pot wall at and slightly below the metal level was cleaned from the lip towards the back of the pot with the vertical edge of the blade. Where much fluid flux had been present on the surface at any stage in the melt or was known to be present in quantity at the bottom of the pot, a layer of fluorspar was applied round the edge of the metal surface in contact with the pot walls before scraping down the latter, and where necessary to the lip itself. In all cases where flux or oxide was being removed from the metal surface, light dusting of Melrasal *E* flux was begun before breaking the metal surface, so as to avoid oxidation, and all scraping of the surface was done from the lip towards the back of pot, from which point the accumulated residue was removed.

Before pouring, the inside of the lip and the pot walls on the pouring side were carefully scraped and the outside brushed with a wire brush. Application of sulphur containing 5% of boric acid was begun and the flux cover cut away from the pot walls at and slightly below the metal surface using a spade-shaped spoon. The flux cover was then pushed back, the exposed metal surface gently skimmed, and the metal poured under a dusting of sulphur alone.

APPENDIX IV.

Note on the Formation of MgF_2 by Pre-Fusion of Fluxes.

It appears generally to have been assumed that when fluxes containing $MgCl_2$ and CaF_2 are melted, interchange of radicals occurs to produce MgF_2 and $CaCl_2$,[6, 15] but, excluding a recent reference in the patent literature (British Patents Nos. 562,597 and 562,636), no evidence of the existence of the change or indication of the extent to which it occurs appears to have been published. Since chloride–fluoride mixtures are usually mutually soluble and appear to be largely ionized, it was not clear what could be meant by a statement that MgF_2 was formed on fusion, other than that the behaviour of a flux when molten depended on the acidic and basic radicals themselves and not on the method of combination in the original flux.

The observation that both the increase in fluidity with temperature and the non-wetting properties associated with fluxes of the Melrasal *MZ*–fluorspar type could be suppressed by excess of $MgCl_2$ (see p. 457), made it evident that some

[*continued on p.* 474.

TABLE V.—*Formation of MgF_2 by Pre-Fusion of Fluxes.*

Ref.	Approximate Composition of Flux before Fusion, %.						Treatment of Flux.	Behaviour in Molten State on Metal at 850° C.	Approximate Composition after Fusion, %.‡				Microscopic Observation of Flux after Pre-Fusion.‖		X-Ray Examination of Flux after Pre-Fusion.	
	$CaCl_2$	NaCl	KCl	$MgCl_2$	CaF_2	MgF_2			CaF_2	MgF_2	Total MgF_2 equivalent to loss in CaF_2 content + original content.	Soluble fluoride as MgF_2.§	CaF_2	MgF_2	CaF_2	MgF_2
A	35	25	17	8	15	Nil	Rapidly cooled from 900° C.	Much more fluid than at 750° C. and strongly non-wetting.	<0·1	2·9	†	11·3 *	None found.	None found.	Absent.	Present.
B	14	10	7	48	21	Nil	Rapidly cooled from 800° C.	Same as at 750° C. Not non-wetting.	2·6	13·8	14·6	0·8	Small amount.	None found.	Present (high crystallinity).	More present.
C	28	21	14	7	Nil	30	Rapidly cooled from 800° C.	Same as at 750° C. Not non-wetting.	<0·1	28·7	30	1·3	None found.	Present.	Absent.	Much present (crystallinity high).
D	10	6	2	48	10·2	11·1	Rapidly cooled from 500° C.	Same as at 750° C. Not non-wetting.	<0·1	17·4	18·3	0·9	None found.	Present.	Not examined.	
	(Balance MgO and impurities.)															

* Reckoned as CaF_2, since $MgCl_2$ not here present in excess. † Not calculated, since $MgCl_2$ not here present in excess.

For notes ‡, §, and ‖, see p. 473.

Notes to Table V.

‡ A special method of analysis was required in order to avoid interchange of radicals on dissolving the sample. Molten fluxes of the type considered will consist of a fluid base, which may contain the "radicals" Na^+, K^+, Mg^{++}, Cl^-, and F^-, and insoluble stiffening agents which may include MgO, CaF_2, and MgF_2. If the melt is rapidly cooled so as to avoid fractional crystallization and then ground and dissolved in water, it is evident that while the CaF_2 and MgF_2 originally present will be unchanged, the fluoride present in solid solution with the chlorides will be precipitated out as a mixture of CaF_2 and MgF_2, if steps are not taken to prevent this. The method used was to dissolve the flux in an excess of Na_2CO_3 solution so that the soluble calcium and magnesium were precipitated as carbonates and not as fluorides. On filtering the solution obtained, the soluble fluoride passed into the filtrate and the original insoluble CaF_2 and MgF_2, together with $CaCO_3$ and $MgCO_3$, remained on the filter. This residue was then treated with dilute acetic acid, when the carbonates dissolved leaving the CaF_2 and MgF_2 in suspension. The analysis was completed by standard methods.

Although only intended for qualitative work, it was evident that roughly quantitative results were obtainable. The following analysis of a synthetic mixture, designed to provide a severe test of the method, indicates the accuracy which may be obtained (Table VI).

TABLE VI.—*Analysis of a Synthetic Mixture Containing MgF_2 and CaF_2 in the Presence of NaF, $CaCl_2$, and $MgCl_2$.*

Constituent.	Weight Taken, g.	Weight Found, g.
CaF_2	0·100	0·103
MgF_2	0·100	0·098
NaF	0·200	...
$CaCl_2$	0·45	...
$MgCl_2$	0·63	...
NaCl	0·30	...
KCl	0·20	...

§ The figure in this column is the difference between the MgF_2 equivalent of the CaF_2 lost on fusion and the insoluble MgF_2 found by analysis; it gives a very rough indication of the order of solubility of MgF_2 in chloride mixtures containing an excess of $MgCl_2$. This appears to be about 1%.

‖ The pre-fused flux was ground, dispersed first in paraffin and then in amyl alcohol, and examined by transmitted and oblique reflected light. In paraffin, the only constituents likely to be present with a refractive index lower than the medium are CaF_2 and MgF_2, and they are readily distinguished, since the refractive index of CaF_2 is close to that of paraffin and the refractive index of MgF_2 is almost equal to that of amyl alcohol. It will be noticed that no MgF_2 was seen in the pre-fused flux where it had been formed by pre-fusion; this is not surprising, since MgF_2 so formed is likely to be in a very fine state of division and small particles cannot readily be examined by Beck's test.[16] MgF_2 has, however, been found in the form of large needles in the flux residues from certain 2-ton melts at Clifton Junction, where the conditions evidently permitted slow precipitation of this substance.

solid compound of melting point greater than 950° C. (the highest testing temperature used) was present in such fluxes when molten. Melting-point data indicated that this could only be CaF_2, MgF_2, or a complex fluoride containing one or both of these substances.

Inspissation of the low-$MgCl_2$ protective base (Melrasal *MZ*) with MgF_2 was found to give fluxes which showed no appreciable increase in fluidity (Fig. 3) or development of non-wetting properties up to 950° C., indicating that MgF_2 was practically insoluble in the Melrasal *MZ* protective base. This suggested that MgF_2 was probably the high-melting compound concerned.

To check this, various pre-fused fluxes were examined by chemical, X-ray, and microscopic methods, and the position of equilibrium in the reaction $MgCl_2 + CaF_2 = MgF_2 + CaCl_2$ was later roughly calculated by approximate thermodynamic methods. Table V gives the effects of pre-fusion on the composition of four typical fluxes as determined by chemical analysis, together with the qualitative results of microscopic and X-ray examination. The procedures for the chemical and microscopic examination are given in notes to the Table.

It will be seen that in the absence of an excess of $MgCl_2$ (flux *A*), the CaF_2 dissolved on fusion of the flux, only a small proportion of MgF_2 being precipitated; the molten flux showed strong non-wetting properties.

In the case of flux *B*, where the protective base was that of Melrasal *E* and $MgCl_2$ was in excess, most of the CaF_2 dissolved on fusion of the flux but was subsequently precipitated as MgF_2. Fusion of flux *D* also resulted in solution of CaF_2 followed by precipitation of MgF_2.

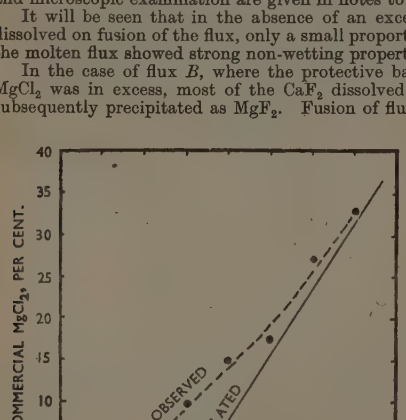

FIG. 4.—Comparison of the Observed and Calculated Minimum Additions of Commercial $MgCl_2$ Required to Suppress the Temperature Sensitivity of Mixtures of Melrasal *MZ* Flux and Fluorspar.

Flux *C*, inspissated with MgF_2, showed no appreciable change on fusion, thereby confirming previous indications of the low solubility of MgF_2 in a protective base of the Melrasal *MZ* type. As stated in the notes to the Table, this solubility is only of the order of 1% at 800° C.

The comparative insolubility of MgF_2 in certain protective bases, such as that of flux *C*, in which $MgCl_2$ is very low or absent, is of considerable practical use in the preparation of fluxes for magnesium alloys containing rare earth metals. Other fluorides cannot be used satisfactorily, even in minor amounts, since they have sufficient solubility to give rise to strong non-wetting tendencies which can only be suppressed by addition of considerable amounts of $MgCl_2$; this latter substance reacts with rare-earth metals and is therefore highly undesirable in fluxes for such alloys. Although MgF_2 also reacts readily with rare earth metals, it is possible to use it for rare earth alloy fluxes because, on melting, the insoluble MgF_2 particles become protected from contact with the metal by a layer of molten chloride. In this way fully inspissated $MgCl_2$-free fluxes [12] have been made, which completely eliminate the flux-inclusion difficulties with cerium-containing alloys which have been experienced in America.[13]

It is interesting to compare the observed and calculated minimum additions of $MgCl_2$ required to prevent mixtures of Melrasal *MZ* with varying proportions of CaF_2 from increasing in fluidity with temperature. As will be seen (Fig. 4), the observed $MgCl_2$ addition necessary to suppress temperature sensitivity agrees reasonably well with that stoichiometrically equivalent to the CaF_2 present: the deviation of the two curves in the region of low CaF_2 concentration, indicating that a considerable excess of $MgCl_2$ is necessary to precipitate small concentrations of fluoride, is in accordance with numerous cases of precipitation in ionizing solvents such as water.

Approximate Calculation of Percentage Conversion at Equilibrium in the Reaction Between $MgCl_2$ and CaF_2.

It is assumed that the following reaction is occurring at 1100° K. (833° C.) between 1 gramme-molecule each of $MgCl_2$ and CaF_2 in a flux of which the other constituents are inert:

$$CaF_{2(s)} + MgCl_{2(l)} = MgF_{2(s)} + CaCl_{2(l)}$$

where the subscripts indicate the physical states of the substances.

Consider first the corresponding reaction where all substances are in their standard states. The increase in heat content or enthalpy of reaction is:

$$\Delta H_{298} = 290{,}200\ ^{20} + 153{,}300\ ^{20} - 263{,}800\ ^{20} - 190{,}600\ ^{20} = -10{,}900 \text{ cal.}$$

The approximate increase in entropy of the reaction is:

$$\Delta S_{298} = -16{\cdot}4\ ^{19} - 21{\cdot}4\ ^{22} + 13{\cdot}6\ ^{*} + 27{\cdot}2\ ^{22} = 3{\cdot}0 \text{ units.}$$

The increase in standard free energy of the reaction (ΔG_{298}) is therefore $-10{,}900 - 3{\cdot}0T = -11{,}800$ cal.

Increments of heat content and entropy between 298° and 1100° K. have been determined for all four substances:

$$\Delta H_{1100} - \Delta H_{298} = -15{,}550\ ^{24} - 25{,}950\ ^{23} + 14{,}450\ ^{24} + 22{,}340\ ^{23} = -4710$$
$$\Delta S_{1100} - \Delta S_{298} = -24{\cdot}65\ ^{24} - 35{\cdot}34\ ^{23} + 22{\cdot}99\ ^{24} + 31{\cdot}24\ ^{23} = -5{\cdot}76$$
$$\therefore \Delta G_{1100} = -15{,}610 + 2{\cdot}76T = -12{,}570.$$

The equilibrium constant K of the reaction is given by the relation $-\Delta G = RT\ln K$, whence $K = 315$.

To calculate roughly the percentage conversion, let x equal the number of gramme-molecules of each reacting substance which have been converted at equilibrium. Then, if the MgF_2 is assumed soluble in the flux, and the activity coefficients are taken as unity:

$$K = \frac{x^2}{(1-x)^2}, \text{ giving } x = 0{\cdot}95.$$

If the MgF_2 is precipitated out and is of negligible solubility but remains in suspension, the value of x is not appreciably affected, though, of course, if the precipitated MgF_2 settles to the bottom of the container and diffusion of dissolved MgF_2 into the reaction zone is slow, x will approach unity. If two molecular proportions of $MgCl_2$ to one of CaF_2 are present initially, x becomes 0·99.

This rough calculation, therefore, indicates that if equilibrium is approached under normal fluxing conditions, substantially all the CaF_2 will be converted to MgF_2 by a stoichiometric equivalent of $MgCl_2$.

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* Estimated from a plot of entropy against the log. of the molecular weight for halides of divalent metals based on data given by Wenner,[19] and also by application of the method of Treadwell and Mauderli,[21] using the known values for CaF_2 and BaF_2.[19]

APPENDIX V.

Notes on Methods for the Detection and Examination of Non-Metallic Inclusions in Magnesium-Base Alloys.

1. *Detection of Flux in Metal by Exposure of a Prepared Surface in the Humidity Chamber.*

In general, the quickest and most satisfactory method of preparing a magnesium alloy surface for flux detection is by machining. If, however, it is desired to ascertain what types of flux are present, it is better to expose a polished surface of the alloy so that development of corrosion spots can be followed microscopically.

(a) *Preparation by Machining.*

If the outside surface of the piece of magnesium to be examined shows adhering moulding sand or any corrosion product, it should first be cleaned with a wire brush or by scrubbing with water or pickling, if necessary.

An assistant, provided with special paper, is present during machining, and his duties are to remove the specimen from the lathe, protect the machined surface with paper and replace it, if a second surface is to be machined. The machining should be finished-off with a very fine cut. After machining, the assistant immediately removes the specimen, wraps it carefully in paper, and carries it to the humidity chamber, where the machined surfaces are gently wiped with cotton wool, using a fresh surface for each pass, before insertion in the chamber.

It is important that each specimen is placed in the humidity chamber as quickly as possible after machining.

A suitable paper has been found to be " brown wrapping paper " (unwaxed *). Some wrapping papers are unsuitable and will tarnish a freshly machined surface after a short period of contact. The cotton wool and paper should be stored away from dust, each piece being used once only.

(b) *Preparation by Micro-Polishing.*

The standard polishing procedure [27] should be followed, except that no alcohol or other solvent capable of dissolving flux must be used and the polishing time should be short.

(c) *Design of Humidity Chamber.*

A glass tank about $14 \times 9 \times 9$ in. with ground rims and a glass plate for covering, forms a suitable chamber. The bottom of the tank is covered with a saturated solution of hypo containing some undissolved crystals. A glass platform is supported above the hypo on a suitable framework made from glass rod. The specimens to be examined are placed on the glass platform, preferably with the machined faces vertical. Where thin slabs requiring support are being examined, it has been found convenient to use a framework of magnesium sheet across which parallel threads of cotton are stretched. Such a device enables slabs to be supported vertically with the minimum of contact. A sheet of cardboard placed on the glass platform prevents the bottoms of the slabs from sliding laterally.

2. *Microscopic Examination of Inclusions.*

Once a corrosion spot has developed after exposing a metal surface in the humidity chamber, it is frequently not possible to identify the type of contamination present, as the corrosion product may mask the underlying structures. In such a case the corroded area should be lightly ground and polished repeatedly until the skins, particles, or other structures which are holding the flux are clearly visible.

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* Supplied by A. Pettitt, Hanover Mills, Buxton Street, Manchester.

By gently breathing on the specimen or exposing it for ½ hr. in the humidity chamber, it will usually be clear from exactly what points of the structure the flux is issuing. Alternatively, CrO_3 solution may be used under a cover glass to indicate the distribution of the flux (see Sub-Section 3. below).

On polishing away the corrosion product from corrosion spots, it is frequently found that the corrosion has preferentially attacked the grain boundaries. Care should therefore be taken not to confuse a cluster of corroded holes and grain boundaries with spider-microporosity.

When examining corrosion spots on metal not exposed under standard conditions, it should be remembered that these may be due to accidental superficial contamination from external sources (Fig. 19, Plate XLVIII), in which case no skins or clusters of particles may be found in the underlying metal. After removal of the corrosion product by light grinding and polishing, the specimen should be exposed for about 48 hr. in the humidity chamber to see whether or not any flux develops. Corrosion spots due to accidental contamination usually contain non-deliquescent dust particles which are readily visible as such under oblique light.

The absence of calcium in corrosion spots on metal which has been treated with standard Melrasal fluxes indicates accidental contamination. The presence of calcium does not, however, prove that the corrosion spot is due to a flux inclusion, because chloride-contaminated dust containing calcium may be present, e.g. in whitewashed foundries.

3. *Detection of Chloride in Corrosion Spots.*

For detecting chloride in corrosion spots, the corrosion product is removed with the clean point of a razor blade and transferred to a clean glass slip. A drop or two of dilute HNO_3, about 5 vol.-%, is added to dissolve metal present and provide the acid required for the test. When solution of the corrosion product is complete, a drop of 1% $AgNO_3$ solution is added, the presence of chloride being indicated by a turbidity of AgCl. The test should always be made alongside a "blank" consisting of scrapings from a clean portion of the metal surface, to ensure absence of appreciable amounts of chloride in the reagents used. The development of the characteristic lace-like turbidity of AgCl is best seen by placing the glass slip on mat black paper. As a check on the chemical nature of the turbidity, it is desirable to add a drop of NH_4OH, which will dissolve AgCl, and to re-precipitate the AgCl with HNO_3.* On stirring, the turbidity clears giving the characteristic "curdy" precipitate of AgCl, which darkens on exposure to light.

When testing corrosion products, in particular those from porous areas near the outside of sand castings, it may be necessary to remove sulphide by heating the acidified solution of the corrosion product before adding $AgNO_3$.

The $AgNO_3$ test as described above will detect 0·2 γ chloride in a corrosion spot, and it may easily be rendered semi-quantitative by use of measured volumes of a dilute chloride solution in the "blank" test. Where spots greater than about 3 mm. dia. are being examined, the comparison may be made in small Nessler tubes.

The CrO_3 test for chloride is more sensitive than the $AgNO_3$ test described, as the CrO_3 can be applied directly to corrosion spots on the metal surface and the results observed under the microscope. CrO_3 is, however, less selective than $AgNO_3$, a weak positive reaction being given in the presence of relatively large amounts of nitrates and sulphates.

A 10% aqueous solution of CrO_3 is suitable. Traces of chlorides are indicated by a vigorous evolution of small gas bubbles from the metal surface and the formation in the presence of larger amounts of chloride of a dark brown stain. The chemical composition of this brown product could not be established by X-ray examination. By applying the CrO_3 in more dilute solution under a cover glass, the presence and distribution of flux along an oxide skin, &c., may be observed under high magnification.

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* The chloride content of the NH_4OH is, however, likely to be greater than that of the nitric acid or the distilled water.

In the presence of carbonates, the CrO_3 reagent also causes effervescence, but it is not difficult to distinguish between carbonates and chlorides in appreciable amounts, because in the former case the bubbles are evolved from the corrosion product and in the latter case from attack on the underlying metal; with carbonates, moreover, the dark stain is not formed.

In view of the extreme sensitivity and imperfect selectivity of chromic acid, it is recommended that anyone using this test for the examination of corrosion spots should first prepare and test spots with various known chloride contents (see Section V. 2. (*b*)), and also test areas of metal which are known by exposure to be flux-free, in order that the indications of the test may be properly appreciated.

4. *Detection of Calcium in Corrosion Spots.*

The following chemical method for detection of calcium in corrosion spots has been used.

The corrosion product after removal from the metal surface, e.g. with a razor blade, is placed on a very small watch-glass with 2 ml. H_2O and one drop glacial acetic acid on a hot plate. When the corrosion product has dissolved and the solution is hot, a few drops of a saturated solution or a small crystal of ammonium oxalate are added. This test was found to give a perceptible precipitate with synthetic corrosion spots containing 10 γ calcium. As with the $AgNO_3$ test, a "blank" test on the reagents should be made with magnesium scrapings and preferably with a very small amount of a flux not containing appreciable amounts of $CaCl_2$, e.g. flux 6 of Table III.

For spectroscopic detection of calcium, the bright lines in the yellow-green at about $\lambda = 5590$ Å were used. With a small laboratory direct-vision spectroscope, used without any "condensing" lens system, it was found possible to detect about 40 γ calcium in a corrosion spot.

5. *Test for Boric Acid in Inclusions.*

The quinalizarin test for boric acid can be used. This reagent gives a reddish-violet colour in slightly diluted H_2SO_4, which is turned blue in the presence of boric acid. As the colour in the absence of boric acid varies from bluish-violet to carmine according to the dilution of the acid, it is essential to control this accurately. It is not possible to dissolve the corrosion product directly in the slightly diluted H_2SO_4 because the hydrogen evolved from adhering metal forms a stable froth in the viscous acid which interferes with the test. The sample must therefore be dissolved in the water used to dilute the acid; the following procedure has proved satisfactory.

A 25-ml. measuring cylinder and a test tube are first rinsed with concentrated H_2SO_4 (sp. gr. 1·84) and the former is filled with 9 ml. of the acid. The sample consisting of corrosion product and metal shavings is brushed into the tube and 1·0 c.c. of water added carefully from a 1-ml. graduated pipette. The tube and contents should be water-cooled to avoid loss of boric acid by volatilization. Solution of the sample may be completed if necessary by pouring a little of the acid from the cylinder into the test tube. When solution is complete, the rest of the acid in the cylinder should be added to the tube and the contents of the latter then shaken and returned to the measuring cylinder. A second 1-ml. graduated pipette is rinsed with concentrated H_2SO_4 and 0·5 ml. of a 0·1% solution of quinalizarin in 93 wt.-% of H_2SO_4 transferred to the cylinder, the contents of which are mixed with gentle shaking and allowed to stand for 5 min. A "blank" test prepared exactly as above using clean magnesium scrapings as a sample should always be made for comparison.

6. *Test for Nitride.*

A drop of Nessler solution applied directly to the metal surface gives an orange-brown precipitate which may take about a minute to develop in the presence of

nitride. Owing to the decomposition of nitride to oxide in damp air, tests for nitride are preferably made on freshly cut surfaces. If the surface is to be given a micro-polish before applying the test, the use of polishing preparations containing water or ammonia must, of course, be avoided.

7. *Test for Sulphide.*

The corrosion product is added to a few drops of water slightly acidified with dilute HNO_3 and a drop of the solution applied to a silver coin. A dark stain develops on the coin in the presence of sulphide. " Sulphur printing " can also be applied.

8. *Test for Iron.*

The corrosion product may be dissolved in a drop of concentrated HCl. A small drop of concentrated HNO_3 is added and several drops of distilled water. On adding a crystal of NH_4CNS, the well known blood-red coloration develops in the presence of iron.

It is important to use only a low HNO_3 concentration, otherwise a similar colour will develop even in the absence of iron. A blank test on a few metal shavings and a trace of flux is therefore desirable. As the presence of flux tends to bleach the red colour, it is desirable to check the sensitivity of the conditions of test by adding to the blank test a drop of dilute $FeCl_3$ solution (e.g. 1 c.c. = 0·0001 g. Fe).

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NON-METALLIC INCLUSIONS IN MAGNESIUM-BASE ALLOYS CONTAINING ZIRCONIUM.* 1166

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Synopsis.

The most effective grain-refining element for magnesium is zirconium, and this is conveniently introduced in the form of an alkali-metal chlorozirconate. Alloys so made are, however, contaminated with flux inclusions, which differ from normal types in that they are not removed by remelting.

A study of these inclusions shows them to consist of the chloride products of the alloying reaction entrapped in clusters of insoluble zirconium-rich particles. These particles are formed through precipitation of dissolved zirconium by certain metallic impurities.

Production of inclusions which are not removed on remelting appears to be a general phenomenon accompanying the introduction into molten magnesium of certain types of elements in the form of reducible chlorides.

Attempts to avoid production of these inclusions and to eliminate them by fluxing, settling, and gauze-filtration methods have been unsuccessful, and it is concluded that zirconium-containing alloys made by alkali-metal chlorozirconates are inherently unreliable from the point of view of freedom from flux and unsuited to commercial development.

Two other special types of flux contamination which are not removable by fluxing, settling, or gauze filtration can arise in zirconium-containing alloys through use of the normal magnesium-base alloy fluxes.

Oxide skins in molten alloys containing zirconium behave in the same way as in "standard" alloys (i.e. pure magnesium and its commercial alloys containing aluminium, zinc, or manganese), but their speed of settling is slower, since they contain precipitated zirconium-rich particles. These particles render them readily detectable by radiography. Dispersed "oxide" in zirconium-containing alloys is not removed by fluxes and may consist largely of ZrN.

I.—Introduction.

In a previous paper dealing with the "standard" ‡ magnesium-base alloys [1] some account was given of the behaviour of non-metallic inclusions in a body of molten metal, and the mechanism of refining with an inspissated flux was discussed. It was concluded that there was no risk under practical conditions of flux inclusions arising in castings from flux suspended in the melt, and that any flux inclusions found in cast metal were due to an unsuitable flux cover or insufficient care in pouring. Such inclusions could readily be removed by simple remelting of the metal.

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‡ This term is used for convenience to denote pure magnesium and its commercial alloys containing aluminium, zinc, or manganese.

So far as is known, these conclusions apply to all commercial magnesium-base alloys with the exception of alloys containing zirconium. It has been found that certain properties of zirconium-containing alloys give rise to special types of non-metallic inclusions, including persistent chloride inclusions which cannot be removed by remelting or flux refinement.

In the course of work on the commercial development of zirconium-containing alloys, Magnesium Elektron, Limited, have developed special alloying methods and fluxes, the use of which avoids at all stages the formation of any of the several types of persistent chloride inclusions which may occur in the zirconium-containing alloys. A brief account of the methods by which the various difficulties met with in this work were overcome has appeared elsewhere.[2] The aim of the present paper is to describe the origin and behaviour of the inclusions characteristic of zirconium-containing alloys and so extend the survey of non-metallic inclusions already given in the paper on standard alloys to cover the whole field of magnesium-base alloys as it appears at present.

A short account of early work leading to the recognition of new types of chloride inclusions associated with zirconium-rich particles is given in Section II. The following Section deals with the nature of the chloride inclusions and the zirconium-rich particles and with the probable manner of their formation. This leads in Section IV to some tentative conclusions concerning the conditions under which persistent chloride contamination is liable to arise when certain alloying elements are introduced into magnesium in the form of reducible chlorides. Section V describes various attempts to remove the chloride inclusions by fluxing, settling, and gauze-filtration methods and to avoid their formation or their passage into the mould during casting.

Two other types of persistent chloride contamination which can arise in zirconium-containing alloys are discussed in Sections VI and VII. Section VIII deals with oxide and nitride inclusions in zirconium-containing alloys, in so far as they show special features not met with in the standard magnesium-base alloys. Some very brief notes of a general nature on the effects of inclusions on the static mechanical properties and corrosion-resistance of magnesium-base alloys are included in Section IX. The main conclusions reached in the paper are set out in Section X.

A few points concerning the examination of castings for flux and the microscopic examination of inclusions, which are of special application to zirconium-containing alloys, are contained in Appendices.

Before outlining the work which led to the recognition of these new types of inclusions, some of the main characteristics of zirconium-con-

taining alloys may be briefly mentioned.[2, 3] Zirconium is soluble in magnesium to the extent of about 0·7% and exerts a pronounced grain-refining action. Thus, while the average grain-size of a 1-in.-dia. chill-cast bar in superheated Elektron A8 alloy is about 0·1 mm., that of the magnesium–zirconium binary alloy is about 0·04 mm., and with the addition of zinc this may be further reduced to about 0·02 mm. It has been found, however, that zirconium will not dissolve in magnesium containing aluminium, manganese, silicon, and certain other elements, because these react with the zirconium to form insoluble high-melting-point compounds.[2, 4] These elements may therefore be termed " alloying inhibitor elements ", and other elements such as zinc and cadmium, which do not interfere with zirconium introduction, may be termed " permissible elements ".

On remelting zirconium-containing alloys, some of the dissolved zirconium is lost and the alloys require " revivification " with more zirconium alloying agent in order to restore the fine grain. Some zirconium loss also occurs if the alloys are held in the molten state for a short time below about 760° C.

Whether the zirconium is added to magnesium in metallic form or as some suitable reducible compound, alloying efficiencies are always low and many undissolved zirconium-rich particles are present in the metal near the bottom of the crucible (Figs. 3, Plate LIII, and 5, Plate LIV).

II.—Early Work Leading to the Recognition of New Types of Flux Inclusions in Magnesium–Zirconium Alloys.

In view of the remarkable grain-refining action of zirconium on magnesium, work on the commercial development of zirconium-containing magnesium alloys was begun in the laboratories of Magnesium Elektron, Limited, in 1939. After some initial difficulties, caused by impurities in the metal and alloying agents used, a method was developed for alloying zirconium by means of sodium chlorozirconate. The chlorozirconate in the form of pre-fused lumps was plunged below the metal surface in a suitable cradle and the melt stirred to effect solution of the zirconium in the magnesium. Because of the low zirconium efficiency of the process, a 12% addition of the alloying salt was required, resulting in the production during the reaction of large quantities of a highly fluid low-melting salt mixture, $MgCl_2.NaCl$. On subsequently casting the alloy, the presence of this fluid residue made it difficult to pour off the alloy completely without fluid salt residue passing into the mould. Attempts were made to stiffen this residue by stirring considerable amounts of

inspissating agents such as CaF_2 and MgO into the melt, but this treatment merely removed fluid alloying residue from the metal surface and had little effect on the consistency of the fluid residue at the bottom of the pot. This initial zirconium alloying process was characterized by a poor metal efficiency and alloys contaminated with chloride inclusions. It was supposed that these inclusions were caused by the large bulk of fluid salt residue and would disappear if the latter could be properly inspissated.

Various methods were developed for inspissating this salt residue. One of the more successful was to prepare at the bottom of the crucible a bath of some protective flux in which CaF_2 is very soluble at high temperatures (e.g. $CaCl_2$ 40, NaCl 30, KCl 20, $MgCl_2$ 10%) and to stir CaF_2 into this at, say, 850° C. until a stiff paste was obtained. The metal to be used for alloying was then charged into the crucible and melted on top of the paste. Such a paste has a very high inspissating effect on a fluid alloying reaction product, since it stiffens by CaF_2 precipitation on cooling to the alloying temperature, about 770° C. On account of the fused chloride coating present on the CaF_2 particles, the paste readily conducts heat and does not interfere with melting of the metal, as does the mere sprinkling of powdered CaF_2 on the bottom of the crucible before melting. In this and other ways complete stiffening of the fluid alloying residue was achieved and this improved the average metal recovery of the zirconium alloying process from 87 to 93%.* It was found, however, that, contrary to expectation, no appreciable reduction in the degree of chloride contamination of the resulting alloys accompanied the stiffening of the fluid chloride alloying residue. Some concurrent experiments on the loss of zirconium occurring on remelting the alloys showed that this chloride contamination was not removed by remelting and fluxing (Figs. 1–2, Plate LII).† At this time, the more sensitive humidity-chamber methods for flux detection, described in the previous paper,[1] had just been developed, and a comparative survey of chloride contamination in standard alloys and zirconium-containing alloys showed the latter to contain much more contamination than had been realized. It was evident, therefore, that the zirconium-containing alloys prepared by the chlorozirconate method were contaminated with flux inclusions of very different behaviour to those occasionally found in standard alloys.

* Approximately 2% of the magnesium is used up in reduction of the $ZrCl_4$, and the balance of the metal, apart from a small melting loss, is either trapped in the stiffened flux residue or is rendered viscous and difficult to cast by the presence of undissolved zirconium-rich particles in suspension.

† See also Ball,[2] Fig. 4.

1. *Extent of Flux Contamination in Zirconium-Containing Alloys Made via Chlorozirconate.*

The extent to which such alloys show chloride contamination depends partly on the scale and conditions of alloying, as will be indicated later. If alloying is carried out on a 10-lb. scale followed by inspissation of the fluid residue in the manner described, and the metal is refined with an inspissated flux such as Melrasal *E* in the normal way for magnesium alloys and then chill cast into a slab, the latter on machining and exposure in the humidity chamber will show very obvious contamination with flux inclusions (Fig. 1). The contamination is particularly gross towards the bottom of the melt (Fig. 2). As the scale of the alloying process is increased, the frequency of the contamination is reduced and on a 2-ton scale it is possible to cast billets which appear to contain little contamination; even so, it is only necessary to machine and expose a few square feet of surface in order to find one or more gross inclusions, which could not fail to give rise to serious local corrosion if exposed to the air during subsequent fabrication of the alloy. The frequency of occurrence of this flux contamination in rolling slabs cast from large melts is discussed in greater detail later.

2. *Microscopic Examination and Classification of Persistent Flux Inclusions Found in Zirconium Alloys.*

A microscopic examination was made of corrosion spots developing on exposure in the humidity chamber of numerous sections cut from zirconium-containing billets and slabs. Chloride inclusions of types I to III [1] were present to a negligible extent, as in standard alloys, and type-IV inclusions occurred rather more frequently than in standard alloys. The large majority of the flux inclusions, however, were seen to be associated with clusters of undissolved metallic zirconium-rich particles and to fall roughly into the following groups :

Type V.—Inclusions of flux up to about 0·5 mm. dia. entrapped in loose clusters of undissolved zirconium-rich particles (Figs. 9–10, Plate LV; see also Figs. 5–8, Plate LIV).

Type VI.—Much smaller amounts of flux more intimately associated with the undissolved zirconium-rich particles themselves (Figs. 7–8, Plate LIV).

Careful small-scale remelting experiments indicated that it was the types of inclusion not met with in standard alloys, namely types V and VI, which persisted after remelting and normal flux refining.

III.—Determination of the Nature and Origin of Chloride Contamination Associated with Zirconium-Rich Particles (Types V and VI).

1. *Nature of the Chlorides Constituting the Persistent Flux Inclusions.*

Examination of the persistent flux inclusions by the chemical and spectrographic methods previously described [1] showed them to be free from calcium. This indicated that the contaminant consisted of the chloride reaction product of the alloying reaction ($MgCl_2$.NaCl) which had not yet settled out, and was not connected with the melting and refining fluxes used or with the bulk of the chloride reaction product at the bottom of the crucible. (The Melrasal fluxes then in use both contained over 30% of calcium halides, and the residue at the bottom of the crucible must also have contained calcium, since the bulk of the melting and refining fluxes used would be present in it.)

In order to obtain, if possible, independent confirmation that the inclusions were unconnected with the fluxes used, attempts were made to contaminate with flux some zirconium-rich particles known to be flux-free. Molten zirconium alloy with the minimum of initial chloride contamination was obtained by careful decantation of the upper layers of metal from a large melt. The zirconium was precipitated with aluminium to produce a considerable number of flux-free zirconium-rich particles and the melt then stirred with fluxes. No observable increase in the degree of flux contamination of the metal took place, indicating that contamination of zirconium-rich particles with melting and refining fluxes does not occur to an appreciable extent.

In view of the existence of "chloride inclusions" which prove to be unconnected with flux, use of the term "flux inclusions" in the remainder of this paper will be confined to chloride-containing inclusions known to arise from the fluxes used, inclusions of alloying reaction product and those of undetermined origin being termed "chloride inclusions".

2. *Nature of the Undissolved Zirconium-Rich Particles Associated with the Persistent Chloride Inclusions of Types V and VI.*

Attempts were made to remove the inclusions by heating the remelted alloys to high temperatures (950°–1000° C.), with a view to dissolving the zirconium-rich particles and so liberating and allowing to settle the entrapped chloride inclusions. These attempts were unsuccessful, indicating that the zirconium-rich particles concerned were insoluble in magnesium and therefore presumably not pure zirconium. Microscopic examination of the zirconium-rich particles associated with the chloride inclusions indicated that they were probably identical in

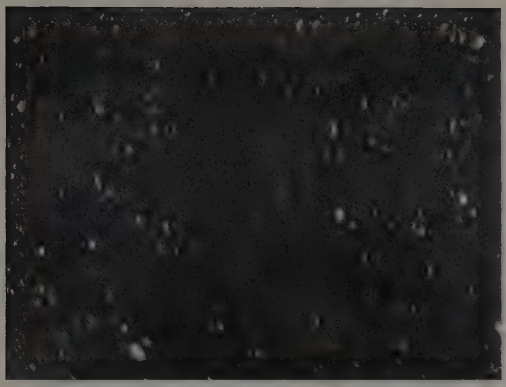
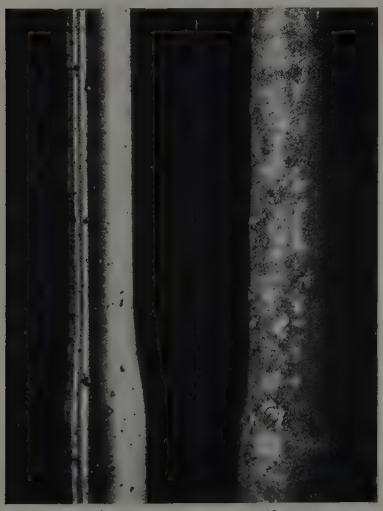


FIG. 1.—Chloride Contamination in a Slab Cast from a 10-lb. Melt of a Magnesium–3% Zinc–0·7% Zirconium Alloy Made *via* Na_2ZrCl_6. (The melt was thoroughly "refined" with Melrasal *E* flux.) × 1.



(*a*) (*b*)

FIG. 2.—Severe Chloride Contamination in Test Bar Cast with Metal from near the Bottom of a Magnesium–3% Zinc–0·7% Zirconium Alloy Melt Made *via* Na_2ZrCl_6.
(*a*) Showing flux development 30 min. after machining.
(*b*) Showing corrosion after 2 days' exposure in humidity chamber. × ¾.

[*To face p.* 486.

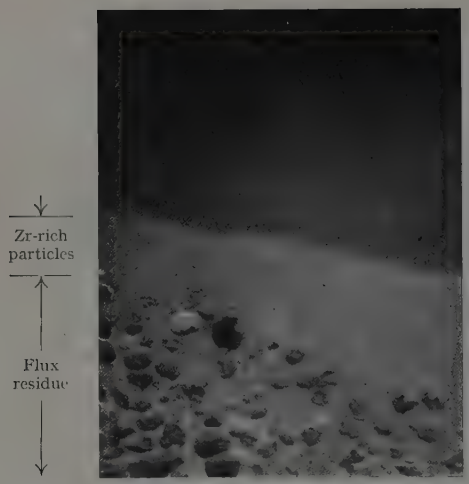


FIG. 3.—Section through Magnesium–Zirconium Alloy Melt Showing Layer of Zirconium-Rich Particles Suspended in the Metal Phase above the Flux Residue. × ¾.

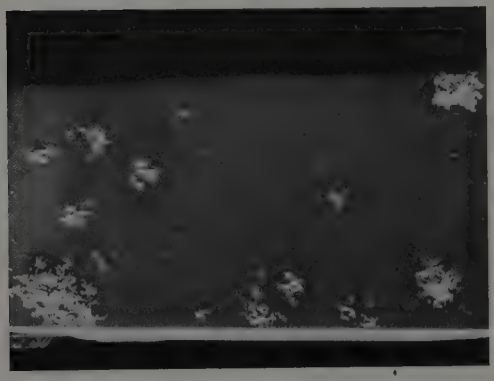


FIG. 4.—Severe Corrosion, Due to Chloride Contamination of Outcropping Microporosity, Developing on a Sand Casting in Elektron A8 after 4 days' Exposure of a Lightly Machined Surface in the Humidity Chamber. Oblique illumination. × 1.

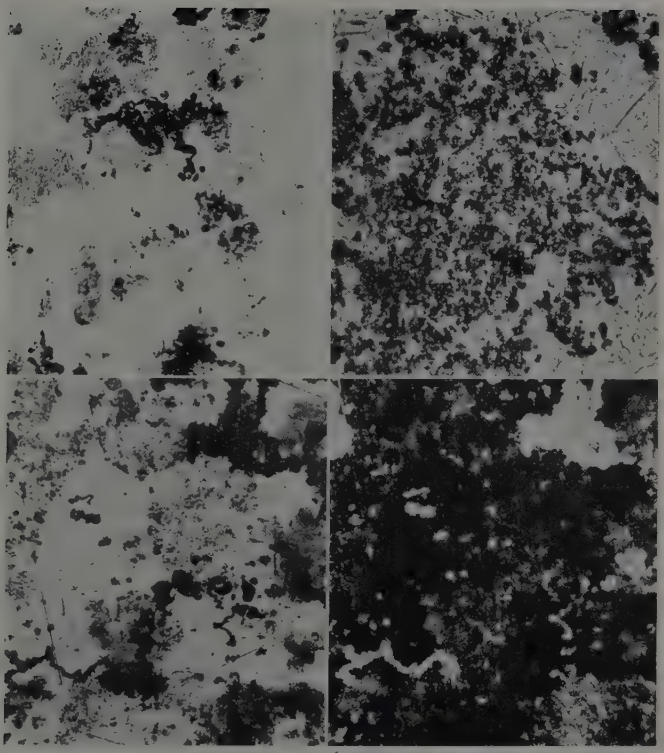


FIG. 5.—Type-V Chloride Contamination : clusters of non-dissolvable zirconium-rich particles from near bottom of a magnesium–zirconium melt after 12 hr. exposure to air of relative humidity = 80%. Note development of heavy local corrosion (black). × 40.

FIG. 6.—Non-Dissolvable Zirconium-Rich Particles. Etched in 2% nital. × 600.

FIG. 7.—Types-V and -VI Contamination. Same specimen as Fig. 6. × 75.

FIG. 8.—Same field as Fig. 7, under oblique illumination. × 75.

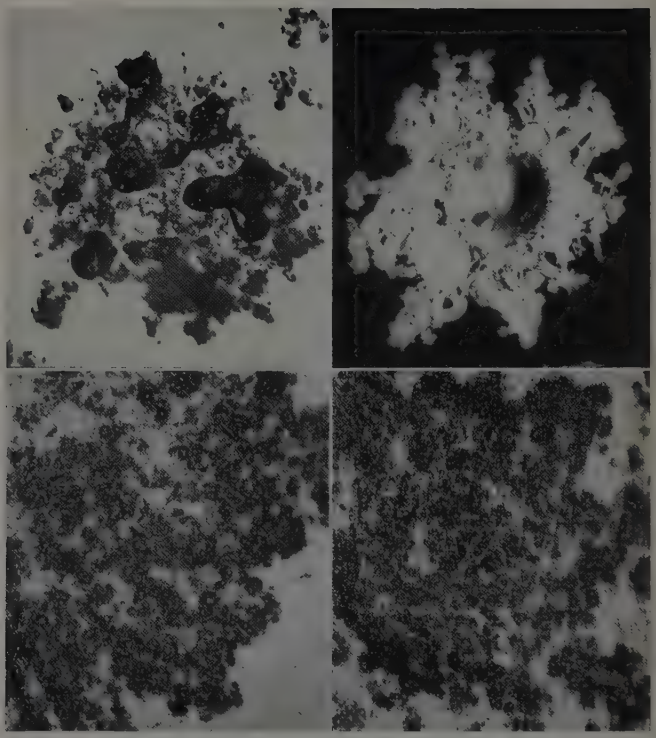


FIG. 9.—Type-V Inclusion. Trapped alloying residue appears black. × 200.
FIG. 10.—Typical Corrosion Spot Developing from a Type-V Inclusion on Exposure to Damp Air. Oblique illumination. × 20.
FIG. 11.—Cluster of Non-Dissolvable Zirconium-Rich Particles in Magnesium–Zirconium Alloy Made *via* $ZrCl_4$. × 500.
FIG. 12.—Cluster of Synthetic Zirconium–Iron Particles Made by Alloying Sublimed Magnesium in a Graphite Crucible with Na_2ZrCl_6 Containing $FeCl_3$. × 500.

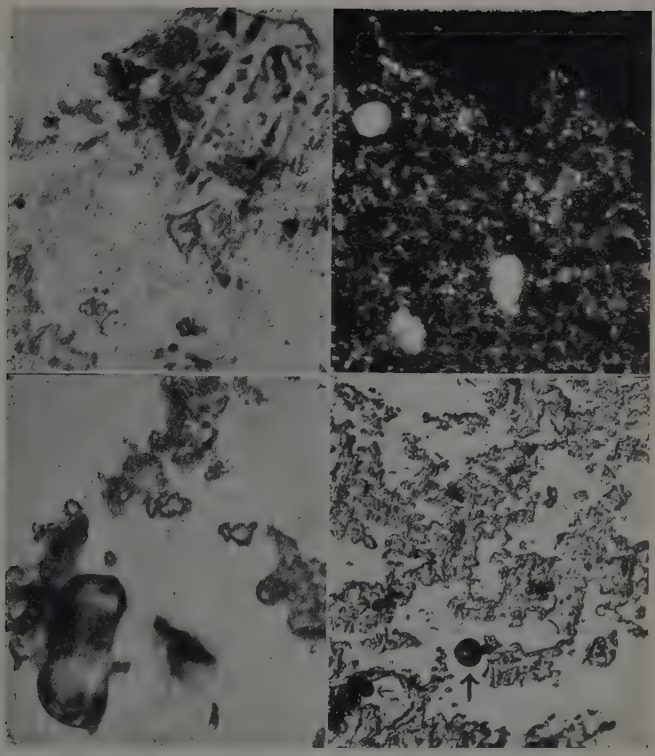


FIG. 13.—Zirconium–Silicon Phase (Dotted Strings). The massive crystals are Mg_2Si. × 500.

FIG. 14.—Tantalum-Rich Particles Formed by Addition of $TaCl_5$ to Magnesium. Note the chloride corrosion after 30 min. in humidity chamber. Oblique illumination. × 20.

FIG. 15.—Synthetic Zirconium–Aluminium Particles Made by Alloying Magnesium Containing Aluminium with Na_2ZrCl_6. Note the deliquescence of included chlorides a few minutes after preparation. × 500.

FIG. 16.—Iron-Rich Phase Contaminated with Chlorides Resulting from Treatment of Magnesium with $FeCl_3$. Note the deliquescence of included chlorides a few minutes after preparation. × 300.

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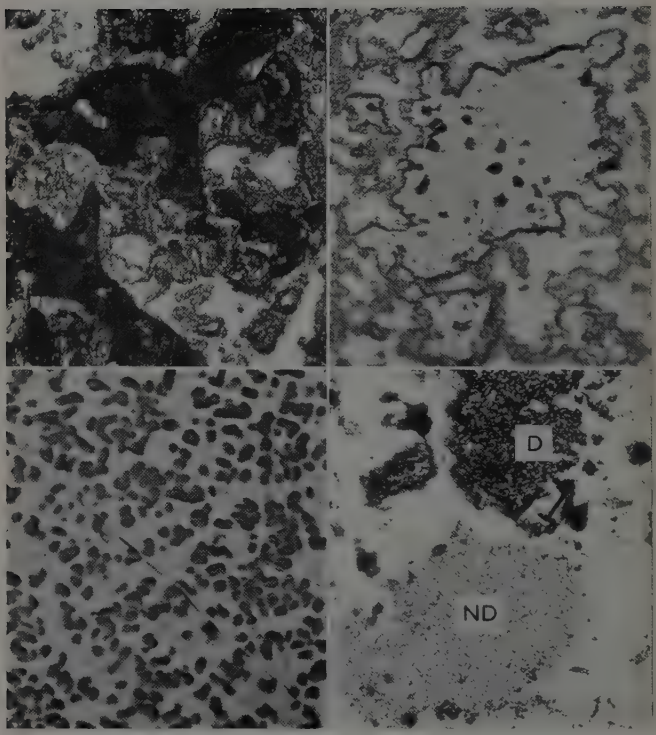

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FIG. 17.—Metallic Zirconium: reaction product obtained from magnesium and ZrF_4 dissolved in inert fluorides, showing strings and sintered masses of metallic zirconium (grey) in magnesium matrix (white) and fluoride alloying residue (black). × 300.

FIG. 18.—Metallic Zirconium in Massive Form Made by Reduction of K_2ZrF_6 with Magnesium. × 500.

FIG. 19.—"Dissolvable Zirconium" Present in the Magnesium Phase of the Reaction Product of Magnesium with K_2ZrF_6. × 600.

FIG. 20.—Dissolvable (D) and Non-Dissolvable (ND) Zirconium-Rich Particles at the Bottom of a Magnesium–Zirconium Alloy Melt Using Excess Alloying Agent. × 300.

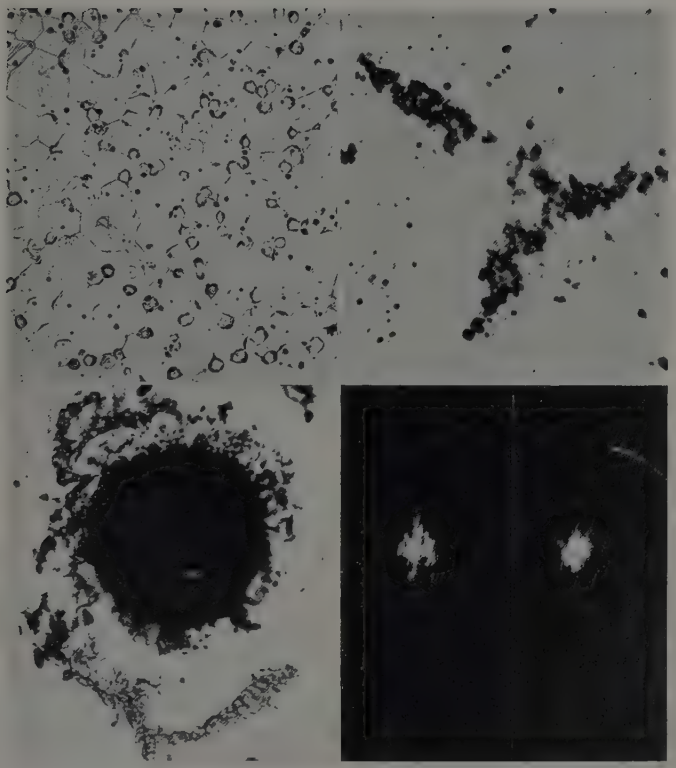

FIG. 21.—Typical Microstructure of Binary Magnesium–Zirconium Alloy Containing 0·6% Dissolved Zirconium. Etched in 2% nital. × 150.

FIG. 22.—ZrN Formed by Stirring a Magnesium–Zinc–Zirconium Alloy in the Pasty State in the Absence of Flux. Etched in 2% nital. × 600.

FIG. 23.—Secondary Chloride Contamination : large circular flux inclusion with appendages. Etched in 2% nital. × 250.

FIG. 24.—Typical Corrosion Spots Developing from the Type of Inclusion Shown in Fig. 23 after 48 hr. Exposure to Air of Relative Humidity = 80%. Oblique illumination. × 1½.

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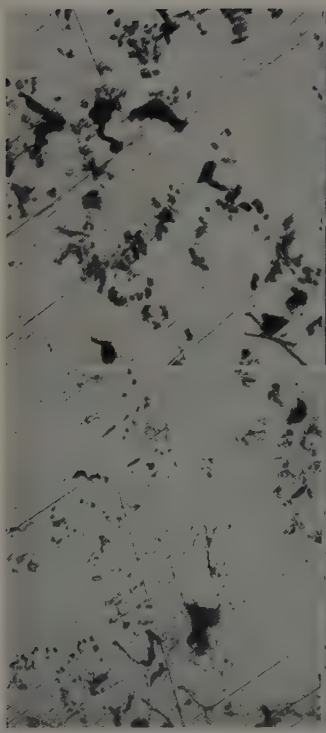

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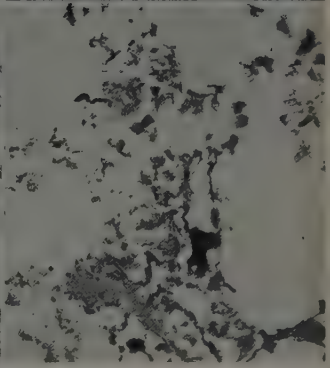

FIG. 25.—Tertiary Chloride Contamination: typical cluster of particles and pores. Etched in nital. × 500.

FIG. 26.—Corrosion Developing from Tertiary Contamination on Exposure for 48 hr. to Damp Air of Relative Humidity = 80%. Oblique illumination. × 15.

FIG. 27.—Tertiary Contamination: zirconium particles, skins, and associated constituent. × 200.

FIG. 28.—Same field as Fig. 27. Etched in 2% nital. × 200.

nature with those present in quantity in the metal at the bottom of the crucible in zirconium alloy melts, whether alloyed with zirconium metal or with chlorozirconates.

Small zirconium-containing alloy melts were made *via* chlorozirconates in thin-walled buckets and quenched after alloying, and the blocks of metal obtained were then sectioned to show the distribution of zirconium-rich particles after various periods of settling. It was found that within a few minutes of alloying, the undissolved zirconium-rich particles had settled into a sharply defined but loosely packed layer at the bottom of the melt, showing much chloride contamination (Figs. 3, Plate LIII, and 5, Plate LIV). Very few particle-clusters remained suspended in the body of the metal, but the particles at the bottom of the crucible were readily disturbed by currents produced in pouring off some of the metal. Remelting of this layer, rich in zirconium particles, with excess of pure magnesium, followed by heating to 950° C., settling, and quenching, gave a block of metal showing little or no grain refinement and at the bottom a thick layer of unchanged zirconium-rich particles still contaminated with chloride.

These zirconium-rich particles, insoluble in magnesium, which occur at the bottom of zirconium alloy melts and which are evidently identical with those associated with chloride inclusions of types V and VI, may be termed " non-dissolvable " zirconium-rich particles.

Preliminary attempts to determine the composition of the non-dissolvable zirconium-rich particles by chemical analysis and X-ray examination gave inconsistent results, until it was decided to extract and examine separately the particles present in the metal and the salt residue at the bottom of the crucible. It was then evident (Table I) that while the zirconium-rich particles entering the flux phase were pure α-zirconium, those in the metal phase were not.

In order to assist in the interpretation of the X-ray patterns, attempts were made to prepare compounds of zirconium with the common alloying inhibitor elements, by extracting the particles from the metal phase obtained in the following melts.

(a) *Zirconium–Aluminium Particles.*

1 kg. of magnesium containing 10% aluminium was melted in a thin-walled bucket, treated at 750° C. with 10% of Na_2ZrCl_6, and the melt quenched after a 5-min. settling period. The settled particles contained zirconium and aluminium roughly in the weight ratio of 2 : 1, and X-ray examination showed the absence of detectable amounts of free zirconium. A strong pattern evidently due to a zirconium–aluminium compound was present.

TABLE I.—*Examination of Zirconium-Rich Particles Recovered from the Metal Phase of Various Experimental Melts.*

Alloying Process (Reacting Substances).	Ref. No.	Composition of Particles.					X-Ray Examination of Particles.								Also Present.	Also Absent.	Remarks.
		Zr, % (approx.)	Al, %	Si, %	Fe, %	Mn, %	α-Zr	Patterns obtained from Synthetic Particles.									
								Zr–Fe	Zr–Si	Zr–Al	Mn	Al	Si	Fe			
Chlorozirconate (Mg/Na_2ZrCl_6)	1	65	6·5	N.D.	20·0	N.D.	*A*	*P*	*A*	*DP*	...	...	...	...	...	Al_2O_3, Fe_2O_3	The presence of some α-zirconium in (2) is attributable to the use of a large excess of alloying agent.
Fluozirconate (Mg/K_2ZrF_6)	2	77	1·4	1·1	4·2	0·97	*P*	*A*	...	...	...	...	...	...	...	Fe_2O_3	
	3	N.D.	N.D.	N.D.	N.D.	0·7	*A*	*PP*	*A*	*A*	...	...	...	...	...	Fe_2O_3	
	4	N.D.	0·44	4·7	25·0	0·58	*A*	*P*	*A*	*A*	...	...	...	...	...	...	
Fluozirconate–chloride (Mg/K_2ZrF_6–KCl–$MgCl_2$)	5	Not analysed.					*A*	...	...	...	...	...	...	...	...	...	Examined for α-zirconium only.
	6						*A*	...	...	...	...	...	...	...	...	...	
Preparation of Zr–Al particles (Mg + Al/Na_2ZrCl_6)	7	56	34·6	N.D.	2·6	N.D.	*A*	...	...	*	...	*A*	...	...	...	MgF_2, ZrO_2, Al_2O_3	
Preparation of Zr–Si particles (Mg + Si/Na_2ZrCl_6)	8	14·6	0·33	11·5	0·3	N.D.	*A*	...	†	...	...	...	*A*	...	$Mg(OH)_2$	Mg_2Si, SiO_2, constituents of zircon sand	
Preparation of Zr–Fe particles (Mg/Na_2ZrCl_6 + $FeCl_3$)	9	64	6·7	1·29	15·7	N.D.	*DP*	‡	...	...	...	...	...	*DA*	...	Fe_2O_3	
(Mg/Na_2ZrCl_6 + AlF_3 + $MgCl_2$)	10	N.D.	13·6	N.D.	N.D.	N.D.	*A*	...	...	§	...	*A*	...	...	...	Al_2O_3, AlF_3	
(Mg/Na_2ZrCl_6 + $MnCl_2$)	11	N.D.	0·25	2·0	7·5	22·4	*A*	*DA*	...	...	*A*	...	...	*DA*	...	Fe_2O_3	
"Dissolvable" Zr (examined in Mg matrix)	12	10	0·01‖	0·04	N.D.	N.D.	Lines other than Mg and Zr very faint.										
Very finely precipitated non-dissolvable Zr-rich particles with dissolvable Zr (examined in Mg matrix)	13	5·0	0·05	0·01	0·33	0·04	Not examined.										

Approx. impurities in materials used:	Al, %.	Si, %.	Fe, %.	Mn, %.	ZrO_2, %.
(*a*) Mg	<0·01	0·01	0·02	0·05	...
(*b*) Na_2ZrCl_6	0·3	0·8	0·2	Nil	1·0
(*c*) Fluxes	0·2	0·6	0·4	Nil	...

* Pattern used for Zr–Al. † Pattern used for Zr–Si. ‡ Pattern used for Zr–Fe. § Very distinct pattern but different from *.
P Present in X-ray pattern. *PP* Present as the major constituent. *A* Absent from the X-ray pattern. *DP* Doubtfully present.

TABLE II.—*Examination of Zirconium-Rich Particles Recovered from the Flux Phase* of Various Experimental Melts.*

Alloying Process (Reacting Substances).	Ref. No.	Composition of Particles.					X-Ray Examination of Particles.								Also Present.	Also Absent.	Remarks.
		Zr, %	Al, %	Si, %	Fe, %	Mn %	α-Zr	Zr–Fe	Zr–Si	Zr–Al	Mn	Al	Si	Fe			
Chlorozirconate (Mg/Na_2ZrCl_6)	1	40	0·83	0·84	10·4	N.D.	*P*	*A*	...	...	...	...	...	...	MgF_2	$Mg(OH)_2$	
	2	Not analysed.					*P*	*A*	...	...	...	...	...	...	MgF_2	$Mg(OH)_2$	
	3	,,					*P*	*A*	...	...	...	...	...	...	$Mg(OH)_2$	MgF_2	
Fluozirconate (Mg/K_2ZrF_6)	4	,,					*P*	*A*	*A*	*A*	...	...	...	...	MgF_2	$Mg(OH)_2$	
	5	,,					*P*	*A*	*A*	*A*	...	...	...	...	MgF_2	$Mg(OH)_2$	
Fluozirconate–chloride (Mg/K_2ZrF_6–KCl–$MgCl_2$)	6	,,					*P*	*A*	*A*	*A*	...	...	...	...	MgF_2, CaF_2		
	7	,,					*P*	*A*	*A*	*A*	...	...	...	...	MgF_2, CaF_2		
Preparation of Zr–Al particles ($Mg + Al/Na_2ZrCl_6$)	8	67	15·1	0·45	1·57	N.D.	*PP*	...	...	*A*	...	...	...	...	MgF_2	ZrF_4, Al_2O_3 AlF	Presence of MgF_2 confirms that AlF_3 took part in the reaction as no CaF_2 used.
Preparation of Zr–Si particles ($Mg + Si/Na_2ZrCl_6$)	9	75	1·1	0·65	0·33	N.D.	*PP*	...	*A*	...	...	...	...	...		Mg_2Si, SiO_2	
Preparation of Zr–Fe particles ($Mg/Na_2ZrCl_6 + FeCl_2$)	10	51	1·63	2·3	0·32	N.D.	*P*	*A*	...	...	...	...	...	*A*		Fe_2O_3, Fe_3O_4, ZrO_2	
	11		0·73	0·46	10·4	N.D.	*P*	...	...	...	...	...	...	...	$Mg(OH)_2$	MgF_2	
($Mg/Na_2ZrCl_6 + AlF_3 + MgCl_2$)	12	N.D.	2·0	N.D.	N.D.	N.D.	*PP*	*A*	...	*A*	...	...	...	...	MgF_2, $Mg(OH)_2$		
($Mg/Na_2ZrCl_6 + MnCl_2$)	13	34	0·16	1·38	3·5	4·7	*PP*	...	...	...	...	...	...	...	MgF_2	$Mg(OH)_2$, ZrO_2	
(Sublimed Mg/purified Na_2ZrCl_6)	14	N.D.	0·48	0·67	N.D.	N.D.	*P*	...	...	...	...	...	...	...	$Mg(OH)_2$	MgF_2	

* The particles extracted from the flux phase are contaminated with acid insoluble impurities from the chlorozirconate and fluxes used, iron scale, &c.
P Present in X-ray pattern.
A Absent from the X-ray pattern.
PP Present as the major constituent.

A note to Tables I and II is to be found on p. 490.

Note to Tables I and II : Methods of Recovering Zirconium-Rich Particles from the Metal and Flux Phases.

(i) *Recovery of Particles from the Metal Phase.*—Metal cast from the extreme end of the pour, or lumps of metal removed from the crucible residue by hand picking, are cleaned by washing in running water, cut into thin slices, weighed, and dissolved in " 15% " hydrochloric acid (15 ml. of concentrated acid of sp. gr. 1·15 to 85 ml. of water). During solution, the calculated volume of concentrated HCl required to dissolve the weight of metal taken is gradually added so as to maintain the concentration of acid.

Maintenance of the proper acid concentration is important, since if this falls below about " 11% " the acid will not dissolve all the zirconium present in solution in the magnesium, and free zirconium will therefore appear in the recovered particles, whether or not zirconium was present in the undissolved state in the original alloy. If the acid concentration materially exceeds the " 15% " specified, chemical attack on the zirconium-rich particles becomes considerable and preferential solution may alter the analysed composition of the particles. Even with the specified composition, the zirconium-rich particles insoluble in the alloy are dissolved by the acid to the extent of about 10%, but for reasons indicated above, a lower acid concentration may not be used when it is intended to examine the insoluble particles for free zirconium. Where free zirconium is not being looked for, appreciable chemical attack on the insoluble zirconium-rich particles may be avoided by dissolving the alloy in concentrated NH_4Cl solution. (1 vol. NH_4OH (sp. gr. 0·880) and 1 vol. H_2O, concentrated HCl being added until the solution is just acid to methyl orange.) Zinc and other alloying constituents may, of course, then be present in the insoluble residue.

When decomposition of the alloy is complete, it is best to wash the particles several times with " 15% " HCl by decantation before collecting them by filtration under suction, as otherwise filtration is extremely slow on account of the viscosity of the concentrated $MgCl_2$ solution. The particles on the filter should be washed with 15% acid, then with water, and dried below about 60° C.

(ii) *Recovery of Particles from the Flux Phase.*—The flux residue is broken up, trapped metal being removed as completely as possible, and added to water which is maintained acid to methyl orange with HCl. When disintegration of the residue is complete, the sludge should be washed through a sieve to remove residual entrapped metal, washed by decantation with slightly acidified water and filtered. The filter cake is also washed with slightly acidified water and dried below about 60° C. If the water in contact with the extracted particles is always maintained just acid to methyl orange, it will prevent contamination of the extracted particles with $Mg(OH)_2$ or a basic chloride, which once precipitated may be rather difficult to re-dissolve without employing an undesirably high acid concentration.

(b) *Zirconium–Silicon Particles.*

1 kg. of magnesium containing 7% silicon, melted as above, was treated at 750° C. with 10% of Na_2ZrCl_6 and the melt settled and quenched. The settled particles contained zirconium and silicon in roughly equal amounts and gave a distinct X-ray pattern indicating the presence of more than one constituent; no free zirconium was found.

(c) *Zirconium–Iron Particles.*

Since iron is only soluble in magnesium to a very slight extent, the iron required to precipitate the zirconium was incorporated as a reducible salt with the alloying agent. 1 kg. of magnesium was first melted and 10% of Na_2ZrCl_6 and 7% of $FeCl_3$, pre-fused together, were then added at 750° C. The settled particles contained zirconium and iron in

the approximate weight ratio of 4 : 1. The X-ray pattern was not clearly defined, but it was evident that free zirconium was substantially absent. A small amount of free iron was possibly present.

Some points of resemblance between these types of "synthetic" zirconium-rich particles and the non-dissolvable particles contained in the metal at the bottom of normal chlorozirconate-alloyed melts may be noted :

(*a*) All three types of synthetic particles were free from α-zirconium (by X-ray examination).

(*b*) All three types were found to be "non-dissolvable" in behaviour : i.e. on remelting with excess of pure magnesium, heating to 950° C., and settling, no grain refinement of the magnesium occurred, and the particles settled to the bottom of the melt unchanged.

(*c*) All three types were contaminated with entrapped chlorides, the severity of the contamination decreasing slightly in the order aluminium, iron, silicon.

Microscopic comparison of the synthetic particles and the "non-dissolvable" particles from zirconium alloy melts indicated that the latter were in all probability zirconium–iron (Figs. 11–12, Plate LV) and zirconium–aluminium compounds, and the presence of the zirconium–iron particles in a number of cases was confirmed by X-ray examination. Most of the X-ray patterns obtained from the non-dissolvable particles were very complex, no doubt because lines due to various compounds of zirconium, aluminium, iron, silicon, and other inhibitor elements were present. Zirconium–silicon particles, which are the most characteristic in microscopic appearance of the three types prepared (Fig. 13, Plate LVI), were found microscopically in considerable quantities in a zirconium melt made in a salamander crucible instead of the usual mild steel crucible.

The results obtained suggest that when a chlorozirconate is added to magnesium, the zirconium which first enters the magnesium phase precipitates alloying inhibitor elements initially present in the metal, and also any alloying inhibitor elements which may enter the metal through reduction by the magnesium of their reducible compounds present as impurities in the chlorozirconate used, e.g. the production of the zirconium–iron particles from pure magnesium and chlorozirconate containing $FeCl_3$. The existence of this latter phenomenon has been confirmed by treatment of magnesium with chlorozirconate containing (i) AlF_3 and $MgCl_2$ ($AlCl_3$ being too volatile to use directly), and (ii) $MnCl_2$. In both cases, flux-contaminated zirconium–aluminium and zirconium–man-

ganese particles, free (by X-ray) from pure zirconium, were formed in the metal phase, while pure zirconium particles entered the flux phase (Tables I and II).

3. *Mechanism of the Alloying Reaction and of Formation of Types-V and -VI Contamination.*

The observation that particles recovered from the flux phase consist substantially of α-zirconium, whether or not the metal or the alloying salt are contaminated with alloying inhibitor elements or their reducible compounds, appears to throw considerable light on the mechanism of the alloying reaction, and the following general picture may be envisaged. The reaction is assumed to occur between molten magnesium and molten chlorozirconate, and for convenience the alloying salt and the non-metallic reaction products are referred to as the "flux phase".

The metallic zirconium which is formed by chemical reaction at the metal–flux interface may either:

(*a*) become wetted by the reaction product and so enter the flux phase in the form of more or less pure zirconium particles, or

(*b*) enter the metal phase.

Entry of zirconium into the flux phase constitutes one of the principal causes of low zirconium efficiency of the chlorozirconate alloying process.

When zirconium particles enter the metal phase, the following events may occur:

(1) Zirconium particles may dissolve in the molten magnesium to give a solution of zirconium in magnesium.

(2) Alloying inhibitor elements, e.g. iron, aluminium, silicon, manganese, originally present in the magnesium used, may precipitate zirconium from solution in the form of insoluble zirconium-rich particles—the "non-dissolvable" zirconium-rich particles (see Figs. 5–6, Plate LIV).

The higher the concentration of alloying inhibitor elements in the magnesium, the greater is the probability that the zirconium dissolving in the magnesium at the metal–flux interface will be precipitated before sufficient time has elapsed for it to become stirred away from the chloride reaction product into the body of the metal. Increase in the concentration of alloying inhibitor elements appears, therefore, to increase the probability that the resulting zirconium-rich particles will be chloride-contaminated.

(3) Salts of alloying inhibitor elements present in the alloying mixture may be reduced by the magnesium and the liberated alloying inhibitor elements alloy with the magnesium and precipitate-out zirconium as

" non-dissolvable " zirconium-rich particles. As the concentration of alloying inhibitor elements introduced into magnesium in this way may be considerable at the metal–flux interface, there seems a greater likelihood of the non-dissolvable zirconium-rich particles formed by this mechanism being contaminated with alloying reaction product than those formed as in (2).

Although chloride inclusions in zirconium alloys made *via* chlorozirconate show almost continuous variation in microscopic appearance from type V to type VI, it is convenient to consider the extreme types separately, as their modes of origin appear to be distinct.

It is believed that type-VI contamination results from processes (2) and (3) above.

Type-V contamination consists of relatively large roughly spherical inclusions of chlorides, which are prevented from settling out rapidly in the molten metal by becoming entrapped in clusters of non-dissolvable zirconium-rich particles (see Fig. 9, Plate LV). When a zirconium melt is held in the molten state, the majority of the non-dissolvable zirconium-rich particles settle out rapidly to form a sharply defined but loosely packed layer in the metal phase at the bottom of the melt. The metal containing the suspended particles is viscous, and any globules of fluid alloying residue which may become detached from the main flux phase during the alloying operation are liable to remain in suspension in this viscous layer, and may be accidentally poured over into castings, especially if several castings are being poured from one melt.

The evidence for this conclusion as to the origin of the gross type-V inclusions is as follows :

(i) Their formation may be largely suppressed by suitable inspissation of the alloying agent before reaction (see Section V. 3.).

(ii) They occasionally contain calcium, indicating a connection with the alloying residue (see p. 486).

(iii) They may be produced under conditions when the suggested mechanisms for production of type-VI contamination cannot operate : e.g. a salt mixture ($MgCl_2.2NaCl$) corresponding to the chlorozirconate alloying reaction product may be placed at the bottom of a crucible, molten zirconium-containing alloy poured on top, and the zirconium precipitated by addition of aluminium. It is found after " puddling " such a melt that some type-V contamination has been produced.

4. *Soluble Types of Zirconium-Rich Phase.*

Before considering the general implications of these views on the mechanism of the chlorozirconate alloying reaction, reference must be

made to two types of soluble zirconium-rich particle which can be produced in magnesium in certain circumstances.

If molten magnesium and molten alloying mixture react under conditions where the non-metallic reaction product is solid or viscous, or if the excess of magnesium used is not large and the melt is not stirred, two more or less distinct zirconium-rich phases may be present in the magnesium-base matrix:

(*a*) Irregular particles and strings of what is in all probability fairly pure metallic zirconium (Figs. 17–18, Plate LVII). This will dissolve in magnesium when the temperature is raised and the non-metallic reaction product has become sufficiently fluid to permit of the melt being adequately mixed. The metallographic appearance and its association with non-metallic alloying residue indicate that this is simply metallic zirconium, formed at the flux–metal interface, which has not yet dissolved in the magnesium. This view is confirmed by the similar habit of manganese and iron introduced into magnesium under similar conditions *via* reducible chlorides. This form of zirconium is rarely found in well stirred zirconium alloy melts and presumably does not therefore contribute to the chloride contamination associated with the use of chlorozirconates.

(*b*) "Dissolvable zirconium" (see Fig. 19, Plate LVII). This is either pure zirconium or possibly a zirconium–magnesium solid solution,* and is apparently formed in the following way. Owing to the heat of reaction, high local temperatures develop in alloying and consequently high local concentrations of zirconium in solution occur, from which "dissolvable zirconium" separates out when the excess local heat is dissipated. This explanation is supported by the observations that dissolvable zirconium is never contaminated with chlorides and that it is practically identical in form and appearance with the zirconium–aluminium phase which separates from a dilute solution of zirconium in aluminium on solidification.

IV.—Tentative Conclusions Concerning the Use of Reducible Chlorides as Alloying Agents.

The views already reached as to the nature and origin of the persistent chloride contamination in zirconium alloys appear to have

* The X-ray patterns given by magnesium and zirconium are practically identical in regard to position of the lines. This phase, which is not readily isolated from the magnesium matrix without decomposition, has been examined in a magnesium matrix and the X-ray pattern was not distinguishable from that of a mixture of magnesium and zirconium. The evidence for the possible existence of a compound Mg_2Zr does not seem to be very strong.[5]

interesting general implications regarding the use of reducible chlorides as alloying agents.

On these views, it would be expected that a flux-contaminated magnesium alloy would result from the introduction into magnesium of any element which is either (case *A*) practically insoluble in molten magnesium, or (case *B*) forms a compound with magnesium or other element present which is practically insoluble in molten magnesium; but that a contaminated alloy would not result where (case *C*) the introduced element is soluble in molten magnesium. This hypothesis may be tested in the case of alloys not containing magnesium, provided the presence of chloride in the resulting alloy can be easily detected by deliquescence or corrosive attack.

To test the hypothesis the following systems have been examined:

Case A.

The introduction of iron into magnesium *via* $FeCl_3$ (see Fig. 16, Plate LVI).

The introduction of chromium into magnesium *via* $CrCl_3$.

The introduction of tantalum into magnesium *via* $TaCl_5$ (see Fig. 14, Plate LVI).

The introduction of molybdenum into magnesium *via* $MoCl_5$.

The introduction of beryllium into magnesium *via* $NaBeF_3$ (+ $MgCl_2$ + KCl).

Case B.

No examples appear to be available apart from those already mentioned, namely the introduction of zirconium as zirconium chloride or chlorozirconate into magnesium containing alloying inhibitor elements, e.g. aluminium, silicon, manganese, and iron, where, as already stated, in all cases heavily contaminated zirconium-rich particles are produced (see Fig. 15, Plate LVI).

Case C.

The introduction of zirconium into aluminium *via* $ZrCl_4$ (+$MgCl_2$).

The introduction of zirconium into zinc (+ magnesium) *via* $ZrCl_4$.

The introduction of zinc into magnesium *via* $ZnCl_2$.

The introduction of indium into magnesium *via* $InCl_3$.

The introduction of thorium into magnesium *via* $ThCl_4$.

In all instances, the results obtained were in accordance with the views stated above.

While no study of the degree and distribution of chloride contamination in alloys coming under case *A* has yet been made, the indications

from small-scale melts are that the contamination is much less serious than in case *B* and is largely confined to the bottom of the melt: this is to be expected, since the chloride is associated with irregular sintered masses and strings of the liberated insoluble element, instead of with a fine precipitate of insoluble particles as in case *B*.

It is, of course, not improbable that where a metal and its chloride differ considerably in density, or the chloride is volatile, persistent chloride contamination of the type considered may not arise.

The case of manganese alloying with $MnCl_2$ does not fall readily into any of the categories *A*, *B*, or *C*, since the solubility of manganese in magnesium, while low, is much greater than that of zirconium and the other elements included in case *A*; and while manganese can be precipitated from solution by iron to some extent, the process is far from complete and, moreover, is therefore likely to be slow. As previously indicated,[1] it is actually observed that AM503 alloy shows a very mild degree of chloride contamination associated with manganese-rich particles, but this is of no practical significance. (See also Table III.)

V.—Attempts to Avoid the Presence or to Effect Removal of Chloride-Contaminated Non-Dissolvable Zirconium-Rich Particles in Zirconium Alloys Made *via* Chlorozirconates.

1. *Attempts to Remove the Contaminated Particles by Fluxing Methods.*

All attempts to remove non-dissolvable zirconium-rich particles by fluxing methods have met with little or no success. Most of the initial experiments were carried out in thin-walled mild steel melting pots of about 8 lb. capacity, so that the melts could be quenched at any stage and the whole block of metal removed by splitting open the melting pot and afterwards examined for distribution of flux and non-dissolvable zirconium-rich particles. Heavily contaminated metal, where required, was obtained from the bottom of large-scale melts or prepared *in situ* by the addition of a small percentage of aluminium followed by chlorozirconate.

After the failure of normal refining flux to absorb or decontaminate the zirconium-rich particles, fluid fluxes were tried, since the particles, although associated with chlorides, were clearly wetted by metal. Various fluid fluxes were employed, such as the melting flux Melrasal *MZ*; $MgCl_2.2NaCl$ (the chlorozirconate alloying reaction product); $MgCl_2$–KCl eutectic (which wets magnesium very readily); NaCl–KCl (which has a low surface tension); and fluid but highly non-wetting fluxes described in the previous paper.[1] These were tried with

or without subsequent stiffening of the flux residue, and in some cases the contaminated metal was poured into a clean pot for refining so as to avoid interference from the bulk of the fluid alloying residue.

As no success was achieved in these experiments, the effect of more intimate contact between flux and metal was studied. Large quantities of $MgCl_2$–NaCl eutectic were stirred into contaminated metal below the liquidus temperature of the latter, so as to produce a uniform paste containing about 15% flux. The paste was slowly remelted, cooled below the liquidus, and the process repeated. Finally, Melrasal *E* flux was applied and the melt taken to 750° C. for 5 min. before pouring. Similar experiments were made with a number of inspissated fluxes prepared by inspissating to various extents both wetting and non-wetting protective bases. Inspissating agents such as MgO and CaF_2, with and without protective chloride coatings, were also tried. In all cases, however, the fluxed metal was found to be still highly contaminated with flux and insoluble zirconium particles. The most that was achieved by fluxing methods was to effect a partial dispersion of the clusters of zirconium-rich particles, thereby reducing type-V but increasing type-VI contamination.

Under the conditions of these tests, it is evident that a far more intimate contact between metal and flux was achieved than is conceivably possible in foundry operation with zirconium alloys, where the metal temperature must not fall below about 760° C., and the possibility of removing the trouble by use of fluid fluxes must now be considered very remote.*

2. *Attempts to Remove the Clusters of Contaminated Particles by Filtration, &c.*

In view of the successful use of steel gauze [6] for removing flux inclusions in the early days of magnesium technology, it seemed worthwhile trying its use for removal of contaminated particles, particularly if some oxide skins were first entangled in the mesh to assist in trapping the particles. Experiments were made with several types of filters, used singly and in series, but although entrapment of a considerable proportion of the chloride inclusions could be achieved, the filtered metal was by no means flux-free. The filtering action of a 16-mesh gauze and entangled fine skins on a flux-free † magnesium–zinc–zirconium alloy melt is indicated in Figs. 29–31 (Plate LX). The

* It has since been learned that the I.G. Farbenindustrie reached a similar conclusion and abandoned work on the alloys containing zirconium because of the flux difficulties.[7]

† Alloyed by the " inert fluoride " process.[2]

retained particles are almost entirely relatively coarse particles of zirconium in dissolvable form which were present because of the use of a large excess of alloying reagent. The finer non-dissolvable zirconium-rich particles have scarcely been retained to any extent.

3. *Attempts to Reduce the Proportion of Zirconium-Rich Particles Produced on Alloying and to Reduce Their Degree of Chloride Contamination.*

Alloying at high temperatures (950° C.), and alloying at normal temperatures followed by superheating the melt for several hours at 950°–1000° C., were found to have no appreciable effect on the flux contamination of the resulting alloy.

Using sublimed magnesium, high purity chlorozirconate, and graphite crucibles and alloying tools, a substantial reduction in the proportion of insoluble zirconium-rich particles produced on alloying was achieved. The reduction in the degree of chloride contamination of the resulting alloys was not, however, such as to encourage search for a commercial solution of the problem along these lines. Moreover, zirconium efficiencies were not as high as with steel crucibles, through precipitation of some dissolved zirconium as carbide.

Various modifications in the composition of the chlorozirconate used for alloying have been tried, e.g. chlorozirconates containing different proportions of NaCl and with and without CaF_2 and $BaCl_2$ additions, mainly with a view to reducing type-VI contamination by modifying the wetting properties of the alloying residue. $BaCl_2$ was added partly to weight the chloride reaction product and so facilitate settling. Briquettes of $ZrCl_4$ with CaF_2, NH_4HF_2, and with magnesium powder, were also tried: the NH_4HF_2 being added with a view to converting the liberated $MgCl_2$ to MgF_2 and so volatilizing the chlorine radical; and magnesium being added with a view to "diluting" the $ZrCl_4$, so as to reduce any tendency for primary zirconium particles to precipitate as the result of local saturation of the metal with zirconium. These experiments were all unsuccessful in preventing or removing type-VI contamination, but it was noticed that with 15% CaF_2 in the chlorozirconate the amount of type-V contamination was considerably reduced and the fluid residue slightly stiffened and agglomerated. This salt mixture was therefore tried out for the revivification of ingot from a 2-ton melt, but the results were disappointing. Introduction of zirconium was impaired by incorporation of CaF_2 into the chlorozirconate, as also occurred in the case of MgO additions. Subsequently, ZrF_4 was tried as an inspissating agent for the chlorozirconate and its use resulted

in satisfactory zirconium introduction and a noticeable suppression of type-V contamination, without, however, causing much reduction in type-VI contamination. The suppression of type-V contamination was most noticeable on small-scale melts, but the effect on 300-lb. melts is illustrated in Tables III and VII.

4. *Attempts to Minimize the Risk of Contaminated Zirconium-Rich Particles Passing Over into Moulds During Pouring.*

A considerable number of experiments have been made to determine alloying or revivifying conditions giving rise to the minimum degree of flux contamination in the resulting alloy. The results obtained were variable, and it is evident that the degree and distribution of the contamination in the castings produced are not under control: e.g. if relatively flux-free zirconium alloy ingot is revivified with 3% chlorozirconate, the resulting castings may be as bad as if the whole of the 12% chlorozirconate addition required by virgin ingot had been added. It therefore appears that no process involving revivification with chlorozirconate before casting is likely to prove successful from the point of view of flux contamination of the final alloy.

In view, however, of the slow and uniform rate of tilting of a 2-ton crucible during the continuous casting of ingot, which might be expected to cause the minimum disturbance of the contaminated zirconium-rich particles at the bottom of the melt, it seemed worth-while to find out whether or not zirconium alloy ingot of satisfactory freedom from flux could be obtained in this way. Two 2-ton zirconium alloy melts were made and cast into ingot, and in each case the ingot showed noticeably less chloride contamination than that cast from medium-scale melts, e.g. 300 lb. Unfortunately, revivification of this ingot in small pots with the minimum addition of alloying salt (3% Na_2ZrCl_6 or 1½% $ZrCl_4$) gave metal showing little improvement in quality over that alloyed in one operation. The reduced degree of flux contamination of the ingots poured from a 2-ton crucible, however, suggested a feasible method for preparing reasonably flux-free billets and slabs, since these could be poured from 300-lb. crucibles filled by careful decantation from a 2-ton crucible, without the need for revivification by fresh alloying agent in the smaller pots.

Experiments have been made to determine the degree of chloride contamination in slabs cast from 2-ton melts in this way. In all cases a normal flux-refining treatment was given to the metal in each 300-lb. pot and in some cases a revivification treatment also. For examination, a proportion of the slabs (24 × 16 × 3 in.) were cut vertically into

TABLE III.—*Average Frequency of Corrosion Spots of Various Sizes for* 100 *cm.*^{2} *Sectional Area of Rolling Slab Cast from* 300-*lb. Pots Filled from* 2-*ton Crucible.*

Alloy.		Treatment in 300-lb. Pot. (Additional to normal flux-refining process.)	Average Number of Corrosion Spots n Falling within Given Ranges of Diameter d per 100 cm.^{2} Sectional Area. Values of d, mm.						Total Sectional Area Examined, cm.^{2}
			1–1½.	1½–2½.	2½–3½.	3½–4½.	>4½.	Σnd^3.	
AM503.		None	0·25 *	Nil	Nil	Nil	Nil	0·3	4,000
Mg–3% Zn–0·7% Zr.	Chlorozirconate alloyed. (Melt No. 3579)	None	0·8	0·85	0·04	0·04	Nil	5	4,600
		Revivified with Na_2ZrCl_6	2·0	1·5	0·05	0·2	0·05	13	2,400
		Revivified with $Na_2ZrCl_6 + ZrF_4$	1·25	0·85	0·085	Nil	Nil	5	3,200
	Fluozirconate § alloyed. (Melt No. 3858)	None	0·4	0·13	0·04	0·025	0·003	1·4	36,600
		K_2ZrF_6/KCl †	0·65	0·45	0·13	Nil	0·01	4	10,400
		Remelted ‡ " pot bottoms " from K_2ZrF_6/KCl melts	3	1·5	1	0·5	Nil	26	4,800

* All associated with manganese-rich particles.

† Directly alloyed in 300-lb. pot.

‡ In order to avoid contaminating the slabs with metal from near the bottom of the pots, nearly one-quarter of the charge was left in the bottom of each 300-lb. pot and separately cast. A special 300-lb. melt of these " pot bottoms " was then made.

§ The " fluozirconate " process is to be regarded as a variant of the chlorozirconate process giving less fluid alloying residues and somewhat less chloride contamination in the resulting alloys. It should not be confused with the successful alloying processes, namely the " inert fluoride " and the " master salt " processes referred to by Ball,[2] which give chloride-free metal (see Table VIII, which gives the results obtained with one of these processes).

strips of approximately 12 × 3 × 3 in. and the two 12 × 3 in. faces, which represented sections across the interior of the slab, were machined and exposed to show flux contamination in the usual manner.[1] As the corrosion spots developing were mostly of comparable thickness, the numbers n of spots of various diameters d were noted and the function Σnd^2 used as a measure of the degree of contamination.

The results of these experiments (Table III) show that even without revivification the decanted metal from the 2-ton crucible is markedly inferior to Elektron AM503 as regards freedom from chloride contamination.

TABLE IV.—*Typical Irregular Distribution of Contamination in a 2-Ton Melt (No. 3858).**

No. of 300-lb. Pot.	Average Number n of Corrosion Spots Falling Within Given Ranges of Diameter d per 100 cm.² Sectional Area. Values of d, mm.						Area Examined, cm.²
	½–1½.	1½–2½.	2½–3½.	3½–5.	>5.	Σnd^2.	
1	...	0·17	...	...	...	0·7	1,200
2	0·33	0·17	0·08	...	...	1·7	1,200
3	0·6	0·25	...	...	...	1·6	1,200
4	0·3	0·06	0·04	0·06	...	2·0	5,400
5	0·23	...	...	...	...	0·2	3,000
6	...	...	...	...	...	0·0	1,200
7	0·17	0·25	...	...	...	1·2	1,200
8	1·25	0·4	0·25	...	...	5·0	1,200
9	0·19	0·04	0·06	0·02	...	1·3	6,000
10	0·75	...	...	...	...	0·75	1,200
11	...	...	...	...	...	0·0	1,200
12	0·7	0·25	0·08	...	...	2·4	3,600
13	...	...	...	...	...	0·0	1,200
14	0·28	0·13	0·07	0·05	0·017	3·0	6,000
15	0·67	0·08	...	...	...	1·0	1,200
16	0·5	0·33	0·17	...	...	3·4	600
Average	0·4	0·13	0·04	0·02	0·003	1·4	36,600 (total)

Note.—From each 300-lb. pot filled by decantation from the 2-ton melt, two rolling slabs approximately 24 × 16 × 3 in. were cast. At least one horizontal slice (area 600 cm.²) was examined from each slab, and in several cases one or both slabs were cut up, 4 slices being taken for examination.

* Mg–3%Zn–0·7% Zr alloyed *via* fluozirconate–chloride method (Mg/K_2ZrF_6–KCl).

In considering the significance of these figures, the important points to bear in mind are the Σnd^2 values and the average numbers of spots of 3 mm. diameter and over. The former indicate the general degree of contamination of the alloy with chlorides. The latter indicate the prob-

ability of exposing gross inclusions in machining or fabricating such as would cause local corrosion, resulting in unfavourable comment and, ultimately, justified condemnation of the alloy by its users, especially in this country where a particularly high standard of freedom from flux in magnesium-base alloys is expected and maintained.

It is also of interest to consider the results given in Table III from a rather different point of view : if instead of cutting up the slabs completely for flux examination a single section only had been taken, what is the probability of this section indicating satisfactory freedom from flux contamination. Such probabilities are shown in Table VII, which gives the percentage of strip faces, each of 200 cm.^{2} area, falling within various ranges of Σnd^2 values. It will be seen that in many cases examination of only one or two machined strips would indicate the alloy to be quite satisfactory from a flux-contamination point of view, and this emphasizes the need to examine a large machined area before any idea of the degree of freedom from chloride contamination of the metal can be obtained.

The highly irregular distribution of the chloride contamination, both in 2-ton melts and also in pairs of slabs cast from the same 300-lb. pot, is shown in Tables IV–VI. Table IV shows irregular distribution of chloride contamination in a typical 2-ton melt and Tables V and VI show irregular distribution of contamination in pairs of slabs cast from 300-lb. pots : Table V represents typical irregularity and Table VI a very exceptional case, where for some reason the first slab poured from the pot appeared to be flux-free and the second slab was highly contaminated.

TABLE V.—*Typical Variation in Contamination Through Two Rolling Slabs Cast from One* 300-*lb. Pot Alloyed* via *Fluozirconate.*

Slab No.	Average Number n of Corrosion Spots Falling Within Given Ranges of Diameter d per 100 cm.^{2} Sectional Area. Values of d, mm.					Area examined, cm.^{2}
	½–1½.	1½–2½.	2½–3½.	3½–5.	>5.	Σnd^2.
3858 (9A) *B*	...	...	...	...	...	0	600
MB	0·17	...	...	...	...	0·2	600
MT	0·5	0·33	...	...	...	2	600
T	0·17	...	...	...	...	0·2	600
(9*B*) *B*	...	...	0·33	...	...	3	600
MB	0·17	...	...	...	...	0·2	600
MT	0·33	...	0·17	0·17	...	5	600
T	0·17	...	...	...	...	0·2	600

Note.—The samples were horizontal slices across the slabs 16 × 3 in., cut from the top (*T*), bottom (*B*), and positions above (*MT*) and below (*MB*) the middle of the slabs. They are entered in the table in the order representing the level of the metal in the pot at the time of pouring.

FIG. 29.—Mechanically trapped particles of metallic zirconium filtered off by the trapped skins.

FIG. 30.—Finer skin and associated precipitated zirconium.

FIG. 31.—Brown lamellated ("pork crackle") constituent trapped by steel gauze, one strand of which appears in part.

FIGS. 29-31.—Section through Residue Left on Wire Gauze Used to Filter a Magnesium-Zinc-Zirconium Alloy Melt. × 100.

[*To face p.* 502.

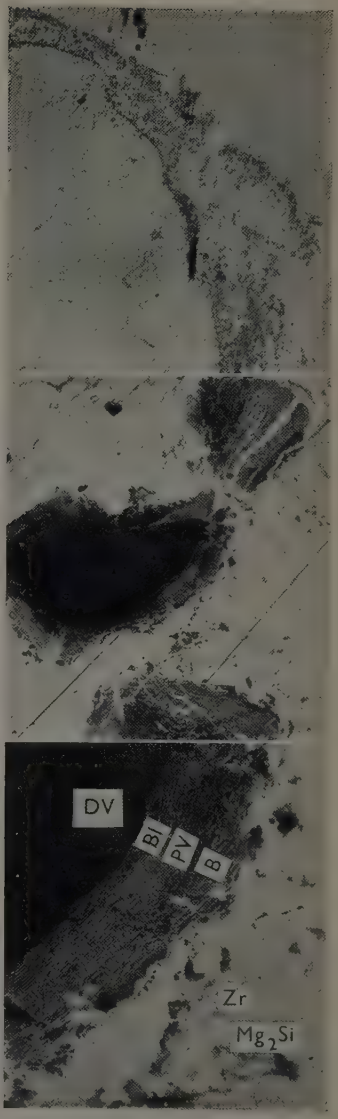

FIG. 32.—Quadrant from a "Ring Nebula" Inclusion Showing Central Fine Skins with Precipitated Zirconium and Surrounding Shell of Metallic Zirconium Particles. × 50.

FIG. 33.—Inclusion Showing Blue Lamellæ. This inclusion was probably produced by reaction with boric acid–French chalk mould dressing. × 150.

FIG. 34.—Same as Fig. 33, Showing Mg_2Si, Secondary Zirconium Precipitation, &c.
DV = dark violet
Bl = blue
PV = pale violet
B = brown × 500.

TABLE VI.—*Primary Chloride Contamination: Exceptionally Irregular Distribution of Contamination in Two Rolling Slabs Cast from One 300-lb. Pot Filled by Decantation from a 2-Ton Fluozirconate Alloyed Melt (No. 3858).*

Average Number of Corrosion Spots n Falling Within Given Ranges of Diameter d per 100 cm.² Sectional Area. Values of d, mm.							Area Examined, cm.²
Slab No.	½–1½.	1½–2½.	2½–3½.	3½–5.	>5.	Σnd^2.	
14*A*	Nil	Nil	Nil	Nil	Nil	Nil	3000
14*B*	0·6	0·3	0·13	0·1	0·03	6	3000

TABLE VII.—*Percentage Distribution of Degree of Contamination* (Σnd^2) *of Machined Strips* (200 *cm.*²) *Cut from Rolling Slab Cast from 300-lb. Pots Filled by Decantation from 2-Ton Crucibles.*

Treatment in 300-lb. Pot. (Additional to normal flux-refining.)	Percentage Distribution of Degree of Contamination Σnd^2 of Strips per 100 cm.² Area.										No. of Strips Examined.
	0–2½.	2½–5.	5–7½.	7½–10.	10–12½.	12½–15.	15–25.	25–37½.	37½–50.	>50.	
None . .	65	13	13	0	0	4	4	...	...	...	23
Revivified with Na_2ZrCl_6 .	37	13	19	13	0	6	0	6	6	...	16
Revivified with Na_2ZrCl_6/ZrF_4	50	17	33	...	...	...	...	...	...	...	12
K_2ZrF_6/KCl* .	66	10	4	4	4	4	8	...	...	...	52

* Directly alloyed in 300-lb. pot.

VI.—SECONDARY CHLORIDE CONTAMINATION IN ZIRCONIUM ALLOYS.

Chloride contamination of types V and VI arising during alloying with chlorozirconates, as previously described, may be termed "primary chloride contamination". It is of interest to see whether or not "secondary chloride contamination" of similar appearance can arise through contamination, by the fluxes used, of the zirconium-rich particles which may precipitate for various reasons from molten zirconium-containing alloys after alloying.

An experiment already described had shown that this secondary contamination, if it occurred, was of an altogether smaller order of magnitude than the primary contamination. The development of the inert fluoride alloying method,[2] where the alloying agent is chloride-free, enabled this question to be examined more closely.

By stirring zirconium-containing alloys with the normal fluxes, two kinds of secondary chloride contamination have been obtained.

(*a*) Occasionally, if considerable quantities of fluxes are stirred down into the alloying residue so that the latter becomes fluid and rich in chlorides, a very light kind of widely distributed contamination can be introduced into zirconium alloys by very prolonged stirring. This form of contamination is probably not of much practical consequence, particularly if the metal is to be worked, and as it is difficult to distinguish microscopically from well-stirred light primary contamination, no distinguishing type number need be allotted.

(*b*) Type-VII chloride contamination: This consists of infrequent spherical inclusions of flux, usually possessing appendages which may be whisker-like in appearance or may resemble the arms of a spiral nebula (see Fig. 23, Plate LVIII). The nature of these appendages is not yet clear. They are barely visible before etching in 2% nital, so that it is probable that they are largely metallic in nature and possibly consist of co-precipitated oxide and metallic zirconium. The appendages are in no way connected with "skins" and show no sign of interface films. Since these inclusions vary from about 0·05 to 0·2 mm. dia., they are capable of forming most objectionable corrosion spots on exposure to damp air (see Fig. 24, Plate LVIII). As with the primary types of contamination, the frequency of occurrence of type-VII contamination was found to decrease with increase in the scale of melting, and Table VIII shows the very low frequency of occurrence of these inclusions in large billets and slabs cast from 300-lb. pots, filled by decantation from 2-ton melts.

TABLE VIII.—*Occurrence of Secondary Chloride Contamination (Type VII) in Billet and Slab Cast from 300-lb. Pots Filled by Careful Decantation from 2-Ton Melts Alloyed by the Inert Fluoride Process Using Normal and Heavy Fluxes.*

2-ton Melt No.	Flux Used on 2-ton Melt.	Treatment in 300-lb. Pot.	Average Number of Corrosion Spots n Falling within Given Ranges of Diameter d per 100 cm.² Sectional Area. Values of d, mm.						Area Examined, cm.²
			1–1½.	1½–2½.	2½–3½.	3½–5.	>5.	Σnd^2.	
3936	Melrasal *E*.	Refined with Melrasal *E*	0·14	0·06	0·04	Nil	Nil	0·8	7,200
		Refined with Melrasal *E* and settled under an "inverse" temperature gradient of approx. 10° C./ft.	0·07	0·008	0·015	Nil	Nil	0·2	12,750
3959	Heavy flux.	Refined with heavy flux.	0·009	Nil	Nil	Nil	Nil	0·01	22,250

Despite the low Σnd^2 value of 0·75, which is almost comparable with that of Elektron AM503 alloy (Table III), such billet cannot be regarded

as satisfactory, for it is clearly only necessary to machine a sufficiently large area in order to expose one or more gross flux inclusions, the reappearance of which in a commercial magnesium alloy would tend to reawaken the general distrust with which these alloys were once regarded.

Attempts to Remove Type-VII Chloride Contamination.

Numerous attempts have therefore been made to remove type-VII inclusions, the work being mainly along the following lines :

(*a*) Modification of known fluxes in various ways, e.g. by adjustment of the $MgCl_2 : CaF_2$ ratio so as to produce a slight non-wetting action.

(*b*) Modification of pouring technique, in particular by fitting special traps to the pouring lip of the crucible and special ingates to the mould.

(*c*) Use of mechanical filters.

(*d*) Use of special inhibitors in place of sulphur, to permit very careful cleaning of the metal surface before pouring and to form a strong coherent oxide tube during pouring.

(*e*) Modifications to the inert fluoride alloying bath, particularly with a view to varying its fluidity.

(*f*) Increase in settling time before pouring.

(*g*) Settling under an " inverse " temperature gradient, i.e. with the top of the melt maintained hotter than the bottom so as to minimize convection.

With the exception of (*g*), none of these methods had an appreciably beneficial effect. Under an " inverse " temperature gradient of approximately 10° C./ft., however, some reduction in frequency of type-VII inclusions was obtained with settling times of 15–20 min. (see Table VIII). This result suggested increasing the density of the fluxes used as a method of overcoming secondary chloride contamination, and it was found possible to devise a series of such fluxes which effectively performed this function (see Table VIII). A comparison with Table III indicates an actual improvement in freedom from flux over standard alloys as represented by Elektron AM503.

VII.—Tertiary Chloride Contamination.

When chloride-free zirconium alloy ingot or scrap is remelted with normal fluxes and revivified, it is found that very light flux contamination, widely distributed, is introduced. This is not the case when a melt of zirconium-containing alloy is allowed to solidify and then remelted, and the effect is therefore evidently a surface one. The flux tends to be associated with loose clusters of precipitated zirconium-rich particles, which differ somewhat in microscopic appearance from those connected with primary contamination. The main characteristic is

that these clusters frequently contain very short lengths of fine skin indicating fragments of a metal–air interface; these skins are absent in primary contamination.

Other features of this tertiary contamination are the more open clusters, the presence of micro-pores, particularly of an elongated or acicular form, and the frequent occurrence of needle-shaped zirconium-rich particles (Figs. 25–26, Plate LIX).

Sometimes the skins found in tertiary contamination are much larger and are associated with a constituent apparently identical with that forming the appendages present in type-VII contamination (Figs. 27–28, Plate LIX; see also Fig. 23, Plate LVIII). This constituent has never been met with except in the circumstances mentioned.

Tertiary contamination, being distinct in origin and nature, therefore constitutes an eighth type of chloride contamination.

No work on the removal of tertiary contamination has been attempted, because the development of the special heavy fluxes mentioned coincided with its discovery, and it was found that use of these fluxes prevented the formation of tertiary contamination.

VIII.—Oxide and Nitride Inclusions.

In origin and behaviour, oxide inclusions in zirconium-containing alloys are very similar to those in standard alloys. Several features, however, call for special mention.

(1) The zirconium-containing alloys are probably slightly more prone to form skin inclusions on pouring than are the standard alloys. It is therefore necessary carefully to clean the metal surface before pouring and to make sure that a proper amount of inhibitor is applied to the pouring stream. With this slight extra care, there is no difficulty whatever in pouring castings in zirconium alloy which are as skin-free as those in standard alloys.

(2) The rate of settling of skin inclusions in a molten body of zirconium-containing alloy is slightly slower than in a body of standard alloy. The reasons for this are probably twofold: the zirconium-containing alloy is slightly more viscous owing to the presence of zirconium not in true solution, and further the skins are associated with zirconium particles which tend to keep them in suspension.

This slower rate of settling of skin inclusions does not, however, result in skin inclusions in castings poured after normal standing and settling periods, and it can be regarded as practically certain that skins found in castings, as with other magnesium-base alloys, have arisen during pouring.

(3) Skin inclusions in zirconium-containing alloys are much more readily detected radiographically than in standard alloys because of the associated zirconium particles. Skin inclusions in zirconium alloys therefore appear as light markings on the negative radiograph.

These particles might conceivably result either from mechanical collection of particles suspended in the melt by the " sweeping " action of the skins, or the zirconium might be precipitated from the alloy by chemical reaction with MgO or Mg_3N_2 in the skin. Microscopic observations indicated that the zirconium particles were frequently very intimately associated with the skins and much smaller in size than primary zirconium, though of the same light colour, in contrast to the general dark colours of the various types of non-dissolvable particle. This suggested that the zirconium was precipitated on or near the skin and was not mechanically collected. To confirm this view, skins were produced in a molten zirconium alloy after the dissolved zirconium had first been precipitated by aluminium. These skins were seen microscopically to have picked up very few particles from the abnormally large number present in suspension, and they appeared dark on the radiograph. None of the finely divided, intimately associated zirconium particles previously observed could be found microscopically, thus confirming their probable formation through precipitation of zirconium by the skin.

By pouring a zirconium alloy melt containing fine skins through a wire gauze, it was found possible to trap the fine skins, which then acted as a filter for retaining suspended zirconium-rich particles: the contrast in appearance between zirconium precipitated on the skins and mechanically filtered zirconium-rich particles is well shown in Figs. 29–30 (Plate LX).

With regard to the mechanism of the precipitation, it is known that of the following reactions:

$$ZrO_2 + 2Mg = 2MgO + Zr \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

$$Zr_3N_8 + 12Mg = 4Mg_3N_2 + 3Zr \quad . \quad . \quad . \quad . \quad . \quad (II)$$

(II) does not proceed much beyond reduction to ZrN and (I) does not go to completion at normal alloying temperatures. It is therefore quite probable that dissolved zirconium will react with MgO or Mg_3N_2 to a slight extent, resulting in the precipitation of particles of zirconium containing oxygen or nitrogen in solid solution. (The presence of a little interstitial oxygen or nitrogen renders metallic zirconium insoluble in magnesium.) While the cause of the zirconium precipitation may therefore well be chemical, it is also probable that these zirconium

alloys, being prepared by exothermic salt reductions, are supersaturated with zirconium which may accordingly tend to precipitate at discontinuities in the melt.

(4) If the zirconium-containing alloys are stirred in the pasty state, much dispersed "oxide" is produced which on remelting settles to the bottom of the crucible (Fig. 22, Plate LVIII). This appears microcopically similar to the corresponding dispersions in the standard alloys,[1] but darkens on etching in nital, suggesting co-precipitation of metallic zirconium. This suggestion is apparently confirmed by the inability of fluxes to remove the suspended "oxide", in contrast to the great ease with which this is achieved in the case of standard alloys.

X-ray powder photographs of a rich suspension of the "oxide" taken from the bottom of a zirconium melt failed to show any pattern other than that due to magnesium, but on chemical extraction of the dispersed particles with strong NH_4Cl solution, the ZrN pattern was obtained.

Since Bruyère and Chauvenet [8] refer to the formation of nitrides by warming ammonia compounds of $ZrCl_4$, which might conceivably arise in the extraction of zirconium-rich particles with NH_4Cl, the presence of ZrN in the original sample was confirmed by X-ray examination of the residue insoluble in dilute acetic acid. It was also confirmed that ZrN is not produced in amounts detectable by X-ray examination on extracting zirconium-rich particles with NH_4Cl by the method given in Note (i) to Tables I and II. The dispersed particles may, therefore, consist of co-precipitated ZrN and metallic zirconium.

Other Non-Corrosive Inclusions in Zirconium-Containing Alloys.

(a) "*Ring Nebulæ*".

These inclusions may be so called from their radiographic resemblance to photographs of ring nebulæ. They consist of a spherical ball of fine skins with associated precipitated zirconium surrounded by shells of primary zirconium-rich particles (Fig. 32, Plate LXI). Such inclusions have so far only been found in large sand-castings where a certain amount of turbulence has probably been present in the running system.

(b) *Brown Lamellated Constituent.*

This is a brown lamellated constituent resembling the "crackle" on pork (Fig. 31, Plate LX). Its composition has not been determined. It has occasionally been found at the centre of a "ring-nebula" type of inclusion.

(c) *Inclusions Due to Mould Dressing.*

Complex inclusions, comprising zirconium–silicon compounds, Mg_2Si, and giving a positive reaction to the boric acid test, have been found to result from accidental flaking of boric acid–French chalk mould dressing.

(d) *Other Types of Lamellated Inclusions.*

Some very remarkable lamellated inclusions have occasionally been noticed in zirconium-containing alloys in which the lamellæ are (i) all brown, as in the type referred to above, (ii) alternately brown and blue, or (iii) alternately an intense blue resembling that of Mg_2Si, and violet (Figs. 33–34, Plate LXI). These inclusions may originate from reaction of the molten alloy with loose particles of moulding sand.

IX.—Note on the Effects of Chloride and of Oxide Inclusions on the Static Mechanical Properties and Corrosion-Resistance of Magnesium Alloys.

Although a study of the effects of inclusions on the mechanical properties and corrosion-resistance of magnesium-base alloys hardly falls within the intended scope of this paper, it may be of interest to record briefly some tentative conclusions which have been reached on the subject.

1. *Mechanical Properties.*

Ultimate tensile strength and elongation are adversely affected by skin inclusions, as is well known, particularly when the skins reach the surface of the test specimen.

There is no evidence to suggest that the flux inclusions occasionally met with in standard alloys have any effect whatsoever on static mechanical properties other than that attributable to associated skins.

Even heavy chloride contamination of the types associated with zirconium-containing alloys is without appreciable effect upon static mechanical properties, and does not interfere with rolling or extrusion of the alloys.

2. *Corrosion-Resistance.*

The effects of normal types of flux contamination on the corrosion of standard alloys are well known.

In the immersion test in 3% NaCl saturated with $Mg(OH)_2$, the adverse effects of the presence of chloride contamination of types VI and VIII are masked by the effect of the zirconium-rich particles with which they are associated, and in general the effects of types-V and -VII contamination, where larger inclusions of chloride are involved, are not pronounced, especially where zinc is present in the alloys.

In atmospheric exposure tests, types VI and VIII have little effect on the results. Types V and VII are more serious and are similar in effect to the normal types of flux contamination occasionally found in standard alloys.

The most corrosive type of chloride contamination under practical conditions, and probably also in any type of corrosion test, is flux-contaminated microporosity (type IV), a severe case of which is shown in Fig. 4 (Plate LIII). Because of its deep-seated nature, removal of the flux from contaminated microporosity by acid pickling, chromate treatment, or boiling in chromate solution is not complete, and corrosion due to residual flux may develop only after some considerable time.

X.—Summary of Main Conclusions.

1. *Primary Chloride Contamination.*

(1) The use of chlorozirconates or $ZrCl_4$ for introducing zirconium into magnesium is accompanied by production of persistent chloride contamination which cannot be removed by remelting or normal flux-refining. This may be termed primary chloride contamination.

(2) Such chloride contamination is unconnected with the fluxes used and consists of the chloride reaction product of the alloying reaction (e.g. $MgCl_2 + NaCl$ from Na_2ZrCl_6) entrapped in clusters of insoluble zirconium-rich particles.

(3) The zirconium-rich particles are alloys of zirconium with one or more of the zirconium alloying inhibitor elements, e.g. aluminium, silicon, iron, and manganese in varying proportions.

(4) During alloying of zirconium with reducible chlorides, much of the zirconium formed at the metal–chloride interface enters the flux residue as pure zirconium particles; zirconium entering the metal phase precipitates, in the form of insoluble compounds, traces of alloying inhibitor elements originally present in the metal, and also alloying inhibitor elements entering the metal phase during alloying, through reduction by the magnesium of their compounds present as impurities in the alloying materials used.

(5) Production of persistent chloride contamination is a general phenomenon resulting from the introduction into magnesium, *via* reducible chlorides, of elements which are either insoluble in molten magnesium or form insoluble compounds with magnesium or some other alloying constituent present.

(6) Two types of soluble zirconium-rich particles are known.

(7) Primary chloride contamination, once formed, cannot be removed completely by fluxing, decantation, or gauze-filtration methods.

(8) The distribution of primary contamination throughout both large and small melts is highly irregular.

(9) Because of primary contamination, magnesium–zirconium alloys made *via* $ZrCl_4$ or alkali metal chlorozirconates are inherently unreliable from the point of view of chloride inclusions and are unsuited to commercial development.

2. *Secondary Chloride Contamination.*

The use of normal fluxes in conjunction with magnesium–zirconium alloys prepared by methods precluding primary chloride contamination gives rise to flux inclusions unassociated with zirconium-rich particles. These inclusions cannot be removed by normal fluxing, decantation, or gauze-filtration methods.

3. *Tertiary Chloride Contamination.*

The remelting of perfectly flux-free zirconium alloy scrap with normal fluxes gives rise to a widespread light form of persistent chloride contamination associated with zirconium-rich particles.

4. *Oxide and Nitride Inclusions.*

(1) The behaviour of oxide skin inclusions in a body of molten magnesium–zirconium alloy is similar to that in standard alloys.

(2) The skins precipitate zirconium in their neighbourhood, which greatly assists in their radiographic detection.

(3) " Dispersed oxide " formed by puddling the alloys in the pasty state readily settles, but, unlike that formed in standard alloys, it is not removed by the normal fluxing process. This " dispersed oxide " appears to consist largely of ZrN and zirconium.

Acknowledgements.

The author's thanks are due to Dr. F. A. Fox, former Chief Metallurgist, and Capt. A. C. Jessup, Chief Metallurgist of Magnesium Elektron, Limited, for helpful discussions during the progress of the investigation; and to Messrs. E. Lardner, J. Nelson, P.A. Fisher, and V. Barak, who carried out some of the experimental work to which reference is made.

The author is indebted to the Directors of Magnesium Elektron, Limited, for permission to publish this paper, and in particular to the Chairman, Major C. J. P. Ball, for his constant personal interest and encouragement.

APPENDIX I.

Note on Segregation of Primary and Tertiary Chloride Contamination.

It is to be noted that the primary and tertiary forms of chloride contamination, namely types V, VI, and VIII, being associated with suspended particles, tend to show segregation effects. This is particularly noticeable in the case of large castings which take a long time to solidify, e.g. large billets. The tendency is for the particles to collect inwards towards the centre and downwards towards the base of a body of solidifying metal. The less the stirring which has been applied to melts, and consequently the smaller the extent to which the clusters of zirconium-rich particles have become broken up and the particles dispersed, the more pronounced is this segregation likely to be.

When a casting is to be cut up for flux examination and a decision is required as to the positions in which it should be sectioned, it may be useful to bear in mind that primary and tertiary contamination are likely to be concentrated in the body of the metal towards the bottom of the casting, whereas contamination due to faulty pouring or, in particular, due to outcropping microporosity, is likely to be situated near the surface of the casting.

APPENDIX II.

Note on the Microscopic Examination of Chloride Contamination in Zirconium-Containing Alloys.

Representative examples of chloride contamination of types V, VI, VII, and VIII should be readily recognizable from the descriptions in the text and the photomicrographs reproduced. Some difficulty may, however, be experienced in determining the nature and origin of light contamination in metal cast from heavily stirred melts, and for this purpose it might be useful to prepare, as comparison standards, blocks of metal each contaminated with a known type of contamination in the unstirred and heavily stirred states. These blocks should, of course, be cast from melts alloyed under such conditions that only the particular type of contamination concerned can arise.

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REPORT OF COUNCIL

for the Year Ended 31 *December* 1948.

THE year 1948 has been one of steady progress for the Institute, and the Council feels that it is one on which they can look back with satisfaction. The reorganization of the Institute's administration, which had partly been completed by the end of the previous year, has been continued, and has made developments in several directions possible.

The Institute's membership has shown a steady net increase, but the total is still not regarded as representative. The President has recently addressed, on behalf of the Council, an appeal to all members to co-operate, both individually and collectively, to bring about a very substantial increase in numbers during 1949, as will be seen from the report on membership on p. 514.

As the Accounts show, the financial position has been much improved, partly owing to the increase in the rate of subscription, and partly to considerable increases in the revenues from advertisements and sales of publications. The past financial year shows a credit balance of £883 against an adverse balance of £2816 in the year 1946–47.

During the year the Council accepted with much gratitude an offer by the Directors of Messrs. W. H. A. Robertson and Company, Ltd., of Bedford, to give the sum of £100 per year, for at least seven years, to provide an award or awards to the author or authors of papers published in the Institute's *Journal* on the engineering aspects of non-ferrous metallurgy. It is hoped that this very generous offer, together with that of Messrs. Capper Pass and Son, Ltd., referred to in the last Report, will stimulate the writing of papers on the processes and plant, and various engineering aspects of the non-ferrous metal industries. There is an erroneous impression that only research papers are acceptable for publication by the Institute. The Council hopes that its acceptance of these generous offers will dispel this impression.

An educational tour for Student Members has been arranged to be held in Birmingham from 4 to 8 April 1949. The Council appreciates the support that has been received for this tour from the Directors of metallurgical concerns in the district. There are indications that the tour will be well attended and will meet a need. If the 1949 tour is successful, others will be arranged each year, either in Great Britain or on the continent of Europe.

It is proposed to organize a series of symposia, to be held at successive Annual General Meetings, on problems of industrial importance. In March 1949 a one-day symposium has been arranged on "Metallurgical Aspects of Non-Ferrous Metal Melting and Casting of Ingots for Working", and a symposium is being organized for 1950 on "The Hot-Working of Non-Ferrous Metals". In November 1949, a symposium will be held, in association with certain allied societies, on "Metallurgical Applications of the Electron Microscope".

The Council has resolved to recommend to the members that the President shall, as a general rule, hold office for one year only, and it proposes to make known each year not only its nominee as President for the next year but also its nominee as his successor. The changes would permit a member to give full attention to the President's obligations for a limited time, and would allow a greater number of members to hold the office. In addition, the next to serve, who would rank as "Senior Vice-President", would have a year in which to obtain an intimate knowledge of the Institute's affairs before he took office, and would act for the President in his absence.

Membership.

A steady growth in membership has been maintained, but the total is regarded as capable of very considerable increase—particularly in industrial metallurgical and engineering fields. At the request of the Council, the President has addressed an appeal to all members to make a serious effort to increase the membership by 1000 during the year 1949, and it is hoped that, as a result, the Institute may become more representative of the world's producers, manufacturers, and users of non-ferrous metals.

A List of Members—the first issued since 1938—was published during the year, and it is hoped to re-issue this list at regular intervals.

The following table shows the growth of membership for the past eight years:

At 31 December	1941	1942	1943	1944	1945	1946	1947	1948
Honorary Members	3	2	6	6	6	6	9	9
Fellows	8	7	7	7	6	6	7	6
Ordinary Members	1862	1866	2018	2153	2213	2414	2491	2546
Associate Members	12	11	15	15	12	25	17	19
Student Members	180	188	267	305	361	529	655	746
Active List	**2065**	**2074**	**2313**	**2486**	**2598**	**2980**	**3179**	**3326**
Suspense List	146	191	195	200	179	58	36	55
Total	2211	2265	2508	2686	2777	3038	3215	3381

Obituary.

It is with much regret that the Council records the deaths of Sir William Murray Morrison, Fellow and Original Member, who served as a Member of Council from 1912 to 1923, and as a Vice-President from 1923 to 1928, and also of Mr. Cyrus Braby and Mr. Arthur Titley, Original Members.

The Council also records, with much regret, the deaths of Dr. C. W. Balke, Mr. Harry Brearley, Mr. J. Drennan, Mr. R. Lloyd Gibbins, Mr. F. F. Gordon, Mr. W. G. Haywood, Mr. R. E. Horley, Mr. J. A. Horne, Mr. F. C. Mannox, Sir Clifford Paterson, Mr. Arthur Smith, Mr. James Smith, and Mr. E. B. Westman.

Officers of the Institute.

The undermentioned members were declared to be elected to fill vacancies as honorary officers of the Institute with effect from the 1948 Annual General Meeting:

President:

Sir Arthur Smout, J.P.

Vice-Presidents:

S. F. Dorey, C.B.E., D.Sc., Wh.Ex., F.R.S.

A. J. Murphy, M.Sc.

H. S. Tasker, B.A.

Honorary Treasurer:

W. A. C. Newman, O.B.E., B.Sc., A.R.S.M., A.R.C.S.

Ordinary Members of Council:
D. F. Campbell, M.A., A.R.S.M.
B. Chalmers, D.Sc., Ph.D.
T. M. Herbert, M.A.
D. P. C. Neave, M.A.
A. R. Powell.

During the year Dr. B. Chalmers resigned his seat on the Council on his departure to take up an appointment in Canada, and, in accordance with the Articles, the Council nominated Mr. H. W. G. Hignett, B.Sc., to fill the vacancy.

Honorary Members of Council.

Captain (E) F. A. Lister, R.N., has replaced Captain (E) J. G. C. Given, C.B.E., R.N., as representative of the Lords Commissioners of the Admiralty; Major-General W. S. Tope, C.B., C.B.E., has replaced Major-General Sir Eustace Tickell, K.B.E., C.B., M.C., as representative of the War Office, and Sir Andrew McCance, D.Sc., A.R.S.M., F.R.S., has replaced Dr. C. H. Desch, F.R.S., as representative of the Iron and Steel Institute. Mr. G. L. Bailey, M.Sc., and Mr. W. E. Ballard have continued to serve as representatives of the Institution of Metallurgists.

The Council desires to place on record its indebtedness to these gentlemen for the services that they have rendered to the Institute.

Corresponding Members to the Council.

The Council wishes to express its appreciation of the help and advice of the following members who have served as Honorary Corresponding Members to the Council during the year: Mr. H. N. Bassett (*Argentina*); Professor J. Neill Greenwood, D.Sc., M.Met.E. (*Australia*); Dr. O. W. Ellis (*Canada*); Professor P. A. J. Chevenard (*France*); Professor N. P. Gandhi, M.A., B.Sc., A.R.S.M., D.I.C. (*India*); Dr. G. H. Stanley, A.R.S.M. (*South Africa*); Professor Dr. C. A. F. Benedicks (*Sweden*); Professor Dr. A. von Zeerleder (*Switzerland*); Professor Dr. N. W. Ageew (*Union of Soviet Socialist Republics*); and Professor C. S. Smith, D. Sc. (*United States of America*).

Institute of Metals Medal.

The Institute of Metals (Platinum) Medal for 1948 was awarded to Mr. Robert Crooks Stanley, M.E., E.M., Hon.Sc.D., Hon.D.Eng., in recognition of his outstanding services to the non-ferrous metal industries.

Publications.

The standard of the Institute's publications has been well maintained, and the volume of matter published has continued to increase. The monthly issues of the *Journal* and *Metallurgical Abstracts* have appeared regularly, and a further considerable increase in the printing order has been made to cover the upward movement of membership and sales.

Very considerable progress has been made in the work of abstracting scientific and technical literature, and members may now expect to have a much more up-to-date service than it was possible to provide during recent years, when there were difficulties owing to the smallness of the abstracting staff and delays in obtaining periodicals.

In the *Monograph and Report Series*, a volume (No. 5) was published containing the papers and discussions of a "Symposium on Internal Stresses in

Metals and Alloys". A sixth, revised, printing has been made of Monograph No. 1: "The Structure of Metals and Alloys", by Dr. W. Hume-Rothery, F.R.S.; a third, revised, printing has been made of Monograph No. 3: "Atomic Theory for Students of Metallurgy", by Dr. W. Hume-Rothery, F.R.S.; and a second printing has been ordered of Monograph No. 4: "An Introduction to the Electron Theory of Metals", by Dr. G. V. Raynor.

The *Annotated Equilibrium Diagrams* continued to be appreciated, and have a steady sale. It is hoped shortly to publish an annotated equilibrium diagram of the system copper–beryllium, by Dr. G. V. Raynor.

Steps have been taken during the year to increase the sales of publications, with very gratifying results. Whereas in the year 1946–47 there was an excess of expenditure over income of £359, the publication accounts during the financial year 1947–48 showed a profit of £677. Sales of Special Publications increased from £630 to £1193.

Meetings of the Institute.

The Fortieth Annual General Meeting, which has been fully reported in the *Journal*, was held in London on 16, 17, and 18 March 1948; visits were made to establishments and works of metallurgical interest.

On 13 May 1948, Professor A. O. Rankine, O.B.E., D.Sc., F.R.S., delivered in London the Thirty-Eighth May Lecture on "The Search for Minerals by Physical Methods".

The Fortieth Autumn Meeting was held in Cambridge from 14 to 17 September 1948; a most gratifying feature was the attendance of members and delegates from overseas. The meeting opened with a service in the Church of St. Edward, King and Martyr, when the Vice-Chancellor of the University (The Rev. Professor C. E. Raven, D.D.) preached a memorable sermon. On the evening of 16 September Professor Sir Lawrence Bragg, O.B.E., M.C., M.A., Sc.D., L.L.D., F.R.S., delivered the Nineteenth Autumn Lecture on "The Cavendish Laboratory".

Joint Meetings.

Joint meetings were held during the year with the British Glaciological Society and the British Rheologists' Club in London on 29 April 1948, when a discussion was held on "The Flow of Ice and Other Solids"; and with the Manchester Metallurgical Society in Manchester on 3 November 1948, when Dr. N. P. Allen, M.Met., gave an address on "Metallurgical Research at the National Physical Laboratory".

Local Sections.

The Local Sections continue to provide a valuable service for members; they have had good programmes, and their meetings have been well attended. Members continue to enjoy the privilege of free membership of the Leeds Metallurgical Society and the Manchester Metallurgical Society.

A pocket programme of the meetings of the Local Sections and of Associated Societies has been published.

The President and the Secretary have paid official visits during the year to the Local Sections and to the Associated Societies. These opportunities for personal contact have been much appreciated.

Metal Physics.

The Metal Physics Committee has met regularly during the year and is organizing a one-day symposium on "Metallurgical Applications of the Electron Microscope", to be held in London in November 1949.

Staff.

The Council expresses its sincere appreciation of the loyalty and devotion to duty of the staff, on which further heavy demands have had to be made during the year.

JOINT ACTIVITIES.

Joint Library and Information Department.

The Library now contains approximately 28,000 volumes and 5000 pamphlets. During the past year a number of important additions has been made to the periodical literature, and every endeavour is made to maintain as complete as possible the collection of metallurgical periodicals and scientific proceedings filed in the Library. Over 200 text-books have been added, many of these by presentation, and the Council thanks those who have presented volumes to the Library.

In 1938, the first complete year of the Joint Library, the number of loans was 2886; in 1948 10,041 volumes were sent out to members, an indication of the great development of the Library services.

Members are reminded that the use of the Lending Library is a valuable privilege of membership. Books and periodicals are sent post free to members resident in Great Britain. In addition to the books filed in the Joint Library, members may borrow through the Librarian, Mr. R. Elsdon, publications from the Science Library at South Kensington. Assistance is also given to all members, in Great Britain and overseas, to obtain photostat copies of articles which can be supplied under certain conditions.

It has not been possible to keep a record of the technical enquiries received, but the work of the Information Department has shown a great increase. The Information Service is prepared to answer scientific and technical enquiries from the members, but it is not its function to give the type of advice which comes within the field of the metallurgical consultant.

Joint Committee on National Certificates in Metallurgy.

The Institution of Metallurgists is now participating with the Iron and Steel Institute, the Institution of Mining and Metallurgy, the Institute of Metals, and the Ministry of Education in operating the scheme for National Certificates in Metallurgy in England and Wales.

Approved schemes for senior courses, leading to an Ordinary National Certificate in Metallurgy, are now in operation at 18 technical colleges, and schemes for advanced courses leading to a Higher National Certificate at 9 colleges.

Final examinations for the Ordinary National Certificate were held during 1948 at 15 of the technical colleges and for the Higher National Certificate at 8 colleges, 123 candidates entering and 74 qualifying for the award of an Ordinary Certificate and 38 candidates entering and 22 qualifying for the award of a Higher Certificate. Distinctions were awarded to 13 candidates who showed exceptional ability in their subjects. Prizes, in the form of books, were awarded to 17 candidates who showed particular merit in the Final examinations, from the Prize Fund established for this purpose by the Iron and Steel Institute, the Institution of Mining and Metallurgy, and the Institute of Metals.

The Joint Committee's Report, with an Appendix giving the Committee's observations and comments on the results of the examinations, after consideration of the Assessors' Reports, has been circulated to the technical colleges concerned, for the assistance and guidance of the Principals and staffs. The Report, Pass Lists, and list of prize-winners, have been circulated to the

participating Institutes and have been or are being published in their Journals.

There has been an increase in 1948 in the number of candidates who entered for the Final examinations for the Ordinary and Higher National Certificate in Metallurgy, and a still greater increase in the number of students entering the first and second years of the courses.

Joint Committee on Metallurgical Education.

Seven meetings of the Committee were held during 1948, including a special one to enable members to meet and exchange views with Professor R. F. Mehl, Chairman of the Advisory Committee on Metallurgical Education of the American Society for Metals.

A second and revised edition of the brochure "Metallurgy—A Scientific Career in Industry" has been published, and contains the latest available information about courses in metallurgy at universities and technical colleges. More than 6000 copies have been distributed to all Local Education Authorities, the Principals of technical colleges, Headmasters of secondary technical schools, and others.

The entrance qualifications to university schools of metallurgy have been considered, and the Committee has published a pamphlet giving its "Recommendations on Qualifications for Entrance to University Schools of Metallurgy", which has been widely circulated to the interested bodies; the recommendations have also been published in the Press and by the participating Institutes.

Parents, careers masters, and others have been provided with details of the educational facilities available to fit boys for various careers in metallurgy, and to make known throughout the Secondary and Public Schools the opportunity offered by metallurgy as a career.

The Committee has recently decided to examine in detail the existing provisions in metallurgical education, and the metallurgical training required, for the different categories of employment—management, research, technical, and operative—dividing its enquiry into two parts: (1) university, and (2) technical college courses. Two Sub-Committees have been appointed for the purpose of this enquiry: (*a*) consisting of representatives of industry and Professors of Metallurgy at the universities, and (*b*) the same representatives of industry with representatives of technical colleges.

Mond Nickel Fellowships Committee.

The Mond Nickel Fellowships Committee held four meetings in 1948, and the following awards were made during the year:

G. S. Campbell (Plessey Company, Ltd.) to study the various stages of the organization from research to large-scale production of specialized metallurgical industries in the United States of America and Canada.

S. J. Garvin (Murex, Ltd.) to study the application of sponsored research, and the administrative methods employed, in the powder metallurgical industries in the United States of America.

A. I. Nussbaum (Thos. Firth and John Brown, Ltd.) to study the application of rolling-mill research, mill plant development, and the theory of rolling to the manufacture of rolled steel products.

The Committee will announce early in 1949 when they will be ready to receive applications for awards for that year.

Sir George Beilby Memorial Fund.

The Administrators of the Fund, representing the Royal Institute of Chemistry, the Society of Chemical Industry, and the Institute of Metals, made awards to Geoffrey Vincent Raynor, M.A., D.Phil., for his researches on the constitution of alloy systems, and to George Reginald Rigby, B.Sc., Ph.D., A.R.C.S., D.I.C., for his researches on refractory materials.

These awards, which had not been made since 1940, are made to British investigators in science as a mark of appreciation of distinguished work, particularly in such fields as fuel economy, chemical engineering, and metallurgy, in which Sir George Beilby's special interests lay.

APPENDIX.

COMMITTEES.

The Committees of the Institute which have served during the year were constituted as follows at 31 December 1948 :

Finance and General Purposes Committee.

Major C. J. P. Ball (*Chairman*).
Professor G. Wesley Austin.
Mr. W. F. Brazener.
Lieut.-Colonel Sir John Greenly.
Sir William Griffiths.
Colonel P. G. J. Gueterbock.
Dr. J. W. Jenkin.
Mr. A. J. Murphy.
Mr. D. P. C. Neave.
Mr. H. S. Tasker.

Ex-officio :

Sir Arthur Smout (*President*).
Mr. W. A. C. Newman (*Honorary Treasurer*).
Dr. L. B. Pfeil (*Chairman, Publication Committee*).

Local Sections Committee.

Mr. W. F. Brazener (*Chairman*).
Professor L. Aitchison.
Mr. J. Cartland.
Professor H. O'Neill.
Mr. A. R. Powell.
Professor F. C. Thompson.

Representatives of Local Sections :

Mr. R. Chadwick (*Birmingham, Chairman*).
Mr. E. H. Bucknall (*Birmingham, Hon. Secretary*).
Mr. W. F. Randall (*London, Chairman*).
Dr. E. C. Rhodes (*London, Hon. Secretary*).
Mr. A. Craig Macdonald (*Scottish, Chairman*).
Mr. Matthew Hay (*Scottish, Hon. Secretary*).
Major F. Orme (*Sheffield, Chairman*).
Dr. W. R. Maddocks (*Sheffield, Hon. Secretary*).
Mr. D. W. Hopkins (*South Wales, Chairman*).
Mr. K. M. Spring (*South Wales, Hon. Secretary*).

Ex-officio :

Sir Arthur Smout (*President*).
Mr. W. A. C. Newman (*Honorary Treasurer*).

Medal Committee.

Sir Arthur Smout (*President*) (*Chairman*).

Ex-officio :

President-Elect.

Ordinary Members :

Not more than four medallists who are, or have been, Members of Council, to be selected by the President.

Metal Physics Committee.

Dr. N. P. Allen (*Chairman*).
Mr. G. L. Bailey.
Dr. Maurice Cook.
Dr. W. Hume-Rothery.
Mr. A. J. Murphy.
Mr. D. A. Oliver (representing the Iron and Steel Institute).
Professor H. O'Neill.
Dr. G. V. Raynor.
Dr. C. J. Smithells.

Ex-officio :

Sir Arthur Smout (*President*).
Mr. W. A. C. Newman (*Honorary Treasurer*).
Dr. L. B. Pfeil (*Chairman, Publication Committee*).

Nominations Committee.

Sir Arthur Smout (*President*) (*Chairman*).
Sir William Griffiths.
Colonel P. G. J. Gueterbock.

Publication Committee.

Dr. L. B. Pfeil (*Chairman*).
Professor L. Aitchison.
Dr. Maurice Cook.
Dr. C. H. Desch.
Colonel P. G. J. Gueterbock.
Mr. T. M. Herbert.
Mr. A. Craig Macdonald.
Mr. A. J. Murphy.
Professor H. O'Neill.
Dr. G. V. Raynor.
Dr. L. R. Underwood.

Ex-officio :

Sir Arthur Smout (*President*).
Major C. J. P. Ball (*Chairman, Finance and General Purposes Committee*).
Mr. W. A. C. Newman (*Honorary Treasurer*).
Dr. N. P. Allen (*Chairman, Metal Physics Committee*).

REPORT OF THE HONORARY TREASURER

for the Financial Year ended 30 *June* 1948.

The accounts which the Council now present cover a year well on into the post-war reconstruction period. They might be expected, therefore, to reflect the progress which the Institute has made in resolving the difficulties of such a period and in picking up the threads of development contemplated in 1939. The re-assumption of full activities, however, is not only a continuance of the ideas and projects of a decade ago, but rather their adjustment to a completely new set of conditions, monetary and otherwise. In this sense it may be said that the Institute has made a satisfactory start and that the peak of immediate anxiety is probably being approached. Financially, the problems of the future cannot be divorced from a still greater expansion of the Institute's activities; the further raising of the present high standing which it has in world metallurgy, so that additional membership may be attracted; and the consolidation of its resources in order that the development of worthy schemes may not be restricted.

The excess of income over expenditure during the year is £883, while the net increases in income and expenditure are £4499 and £800, respectively. Last year, it may be recalled, expenditure exceeded income by £2816, which the Council met by a transfer from the War-Time Emergency Fund. In addition, the Council suggested the raising of the subscription, which accounts for most of the increase in the income.

Where last year there were losses of £342 and £17, respectively, on the *Journal* and *Metallurgical Abstracts* and Special Publications accounts, this year income exceeds expenditure by £351 and £326.

Expenditure, as a whole, follows closely the estimates made earlier in the year. An item of £330 has been included for the cost of a new list of members.

The Balance Sheet has been prepared in accordance with the Companies Act, 1948, and is intended to show more clearly those funds which are held mainly for income from interest and those which are more fluid and available for use as required.

In the General Fund the investments show a decline of £1409, which was due partly to the sale of stock to meet the overdraft shown in last year's accounts. Unpaid subscriptions amount to the very high figure of £961, an increase of £263 over that for 1946–47. It cannot be too strongly emphasized, once again, that prompt payment of subscriptions, preferably by Bankers Orders, is of considerable benefit to the Institute and a great help to its officers.

The War-Time Emergency Fund, which last year was drawn upon to the extent of £2816 in order to meet a deficit, has this year been used to provide advance payments for publications to be issued in 1948–49. Such sums will ultimately be returned to the War-Time Emergency Fund from the various publication accounts.

The overdraft of £398 at the Bank represents mostly unpresented cheques. The overdraft of £2129 at the end of the previous year has been met partly by the sale of stock and partly from revenue.

The reserves are greater than last year by £620, while current surpluses consisting of the Accumulated Fund, the War-Time Emergency Fund, and the Special Publications Reserve have increased by £1030 to £14,313. Current liabilities are £990 less, at £2437.

The beginning of the year was one of some anxiety with regard to the investments. The very wise precautions taken by Mr. Tasker to convert War Loan and Consol holdings, which were then on a falling market, into Railway Stock having fixed prices on January 1st preserved the capital structure of the Institute which has always been the aim of the Council. Subsequent exchange into Transport Stock and the sale of this to buy 4% Consols and 2½% National War Bonds whose price levels, it was considered, would not fluctuate violently, resulted in a loss of £707. Overall, however, there was a gain in all these transactions of £484.

The Council has adopted the Auditors' recommendation that the accounts of the Mond Nickel Fellowship Fund and of the Capper Pass Fund, for each of which the Institute is in the position of Trustee, should be included in the Institute accounts as "Special Funds".

It has also been agreed that £5000 shall be transferred from the amount standing under Current Surpluses to General Reserve.

The 4% Consolidated Stock now held by the Institute was bought at a price above par and is repayable in 1957 or after. It has therefore been decided to create a Sinking Fund of £250 per annum to cover the loss on redemption of this Stock.

THE INSTITUTE OF METALS.

SCHEDULE OF SECURITIES, 30 JUNE 1948.

30.6.47. £	£		£	s.	d.	£	s.	d.
		General Fund :						
	5,500	£5,500 3% Savings Bonds, at cost	5,500	0	0			
	1,010	£1,010 2½% Treasury Stock, at cost	1,010	0	0			
	—	£4,359 4% Consolidated Stock, at cost	4,734	6	11			
	—	£5,000 2½% National War Bonds, at cost	5,057	1	0			
	4,822	L.N.E.R. 4% 2nd Guaranteed Stock		—				
	6,378	Southern 5% Guaranteed Stock		—				
17,710						16,301	7	11
		Endowment Fund :						
	1,000	(3%) £525 2½% Defence Bonds, at cost	525	0	0			
	1,285	£1,285 3% Savings Bonds, at cost	1,285	0	0			
	—	£17,926 4% Consolidated Stock, at cost	19,482	7	4			
	7,563	L.N.E.R. 3% Debenture Stock		—				
	233	Southern 5% Guaranteed Stock		—				
	5,215	L.M.S. 4% Guaranteed Stock		—				
	5,114	L.M.S. 5% Guaranteed Redeemable Preference Stock, 1955		—				
20,410						21,292	7	4
		War-Time Emergency Fund :						
	1,000	(3%) £500 2½% Defence Bonds, at cost	500	0	0			
	375	500 15*s.* War Savings Certificates, at cost	375	0	0			
	150	150 £1 War Savings Certificates, at cost	150	0	0			
	950	£950 2½ National War Bonds, at cost	950	0	0			
	—	£795 4% Consolidated Stock, at cost	880	0	0			
	1,950	3% Savings Bonds		—				
4,425						2,855	0	0
£42,545						£40,448	15	3

THE INSTITUTE

BALANCE SHEET AS

30.6.47. £	£	£		£ s. d.	£ s. d.	£ s. d.
			RESERVES.			
	20,987		*Endowment Fund*	21,294 9 10		
			General Reserve:	£ s. d.		
	5,000		Balance as at 30 June 1947.	5,000 0 0		
			Add Transfer from Accumulated Fund	5,000 0 0		
				10,000 0 0		
			Entrance Fees:			
		3,772	Balance as at 30 June 1947	4,055 13 11		
		284	Amounts receivable during year	311 6 6		
	4,056			4,367 0 5		
30,043					35,661 10 3	
			CURRENT SURPLUSES.			
			Accumulated Fund:			
	7,393		Balance as at 30 June 1947.	7,393 7 9		
			Add Excess of Income over Expenditure for the year	883 3 10		
	2,816		*Less* Excess Expenditure	—		
	4,577			8,276 11 7		
				£ s. d.		
			Less Transfer to General Reserve	5,000 0 0		
			,, Transfer to Investment Redemption Reserve	250 0 0		
				5,250 0 0		
	2,816		*Add* Transfer W.T.E. Fund.			
				3,026 11 7		
	7,393					
	5,144		*War-Time Emergency Fund*	5,286 16 11		
	750		*Special Publications Reserve*	750 0 0		
13,287						
			Investment Redemption Reserve	250 0 0		
					9,313 8 6	
			CURRENT LIABILITIES.			
	779		Sundry creditors	1,551 17 4		
	278		Subscriptions paid in advance	486 18 9		
	2,129		Lloyds Bank, Ltd.—overdrawn	397 18 6		
					2,436 14 7	
	240		Due to War-Time Emergency Fund.			
3,426						
			SPECIAL FUNDS.			
	7,000		*Mond Nickel Fellowship Fund*	13,858 11 8		
	—		*Capper Pass Fund*	200 0 0		
7,000					14,058 11 8	
£53,756					£61,470 5 0	

REPORT TO THE MEMBERS OF THE INSTITUTE OF METALS.

We have audited the above Balance Sheet dated 30 June 1948, and the annexed Income and Expenditure Account for the year ended 30 June 1948, and report that we have obtained all the information and explanations which to the best of our knowledge and belief were necessary for the purposes of our audit.

In our opinion, proper books of account have been kept by the Institute, so far as appears from our examination of those books.

The above mentioned Balance Sheet and annexed Income and Expenditure Account are in agreement with the books of account. In our opinion, and to the best of our information, and according to the explanations given us, the said Accounts give the information required by the Companies Act 1948, in the manner so required, and give a true and fair view, in the case of the Balance Sheet of the state of the Institute's affairs as at 30 June 1948, and in the case of the Income and Expenditure Account of the excess of income over expenditure for the year ended 30 June 1948.

POPPLETON & APPLEBY,
CHARTERED ACCOUNTANTS,
BIRMINGHAM AND LONDON.

15 *September* 1948.

Approved on behalf of the Council:

ARTHUR SMOUT, *President.*
W. A. C. NEWMAN, *Honorary Treasurer.*
C. J. P. BALL, *Chairman, Finance and General Purposes Committee.*
S. C. GUILLAN, *Secretary.*

OF METALS.

AT 30 JUNE 1948.

30.6.47. £	£	£		£ s. d.	£ s. d.
			FIXED ASSETS.		
			Office Furniture :		
		1	Nominal value as at 30 June 1947	1 0 0	
			Additions during Year, at cost	326 3 5	
				327 3 5	
			Less Depreciation	21 8 8	
				305 14 9	
			Library Books, &c. :		
		1	Nominal value as at 30 June 1948	1 0 0	
		2			306 14 9
			INVESTMENTS AND FUNDS.		
			General Fund :	£ s. d.	
		17,710	Securities at cost, per schedule	16,301 7 11	
			(Market value £16,213 18*s.* 2*d.*)		
			Lloyds Bank, Ltd., Deposit Account		
		16		31 7 [illegible]	
		2	Post Office Savings Bank	5 5 2	
		17,728		16,338 0 9	
			Endowment Fund :		
		20,410	Securities at cost, per schedule	21,292 7 [illegible]	
			(Market value £21,368 12*s.* 4*d.*)		
			Lloyds Bank, Ltd., Deposit Account		
		577		2 2 6	
		20,987		21,294 9 10	
			War-Time Emergency Fund :		
		4,425	Securities at cost, per schedule	2,855 0 0	
			(Market value £2,924 16*s.* 0*d.*)		
			Lloyds Bank, Ltd., Deposit Account		
		122		961 10 4	
		357	Post Office Savings Bank	7 10 0	
			Lloyds Bank, Ltd., Current Account		
		—		569 3 0	
			Payments in advance for publications		
		—		886 10 5	
		—	Income Tax Recoverable	7 3 2	
				5,286 16 11	
		240	General Fund.		42,919 7 6
		5,144			
		43,859			
			CURRENT ASSETS.		
			Stock of Journals and Special Publications, at nominal value	1 0 0	
			Debtors :	£ s. d.	
		698	Unpaid Subscriptions	961 6 10	
		65	,, Entrance Fees	68 5 0	
		763		1,029 11 10	
			Less Reserve for Doubtful Subscriptions and Entrance Fees		
		334		151 6 5	
		429		878 5 5	
			Sundry Debtors and Payments in		
		1,282	Advance	3,106 5 [illegible]	
			Advance to the Institution of		
		250	Metallurgists	200 0 0	
		1,961		4,184 11 1	
		12	Cash in Hand.		4,185 11 1
		921	Special Publications Savings Bank.		
		933			
		2,895			
			INVESTMENT OF SPECIAL FUNDS.		
			Mond Nickel Fellowship Fund :	£ s. d.	
		—	Abbey National Building Society	5,000 0 0	
		—	Halifax Building Society	1,250 0 0	
			Co-operative Permanent Building		
		—	Society	1,250 0 0	
		—	Post Office Savings Bank	500 0 [illegible]	
		—	London Trustee Savings Bank	500 0 0	
		3,850	Lloyds Bank, Ltd.—Deposit	2,208 11 [illegible]	
				10,708 11 8	
		3,150	Income Tax Recoverable	3,150 0 [illegible]	
		7,000		13,858 11 8	
			Capper Pass Fund :		
		—	Post Office Savings Bank	200 0 0	
		7,000			14,058 11 8
		£53,756			£61,470 5 0

THE INSTITUTE OF METALS.

INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 30 JUNE 1948.

30.6.47.		EXPENDITURE.	£ s. d.	£ s. d.
£	£			
6,130		To Salaries, Wages, and National Insurance	6,110 12 0	
520		,, Superannuation Fund	610 6	
438		,, Pensions to former Staff	516 0 0	
134		,, Lighting and Heating	149 13 4	
769		,, Rent, Services, and Insurance (including *ex gratia* payment for services of £100)	878 0 0	
531		,, Postage, Despatch and Telephone (*less* Receipts)	639 10 2	
771		,, Printing and Stationery	680 16 4	
86		,, Sundry Expenses	108 19 4	
87		,, Council and Committee Expenses	142 15 3	
—		,, Official Entertaining	92 6	
279		,, Staff Travelling and Secretarial Expenses	280 9 3	
500		,, Joint Library Contribution	500 0 0	
17		,, Subscriptions and Presentations	80 14 6	
197		,, Grants to Local Sections and Associated Societies	169 5 0	
383		,, Meeting Expenses (including Reporting), *less* Receipts	548 15 4	
183		,, Repairs and Renewals of Furniture and Equipment	170 14 4	
—		,, Depreciation of Furniture and Equipment	21 8	
33		,, Bank Charges, *less* Interest	49 6 3	
37		,, Audit Fee	36 15 0	
10		,, Professional Charges	148 1 0	
325		,, Joint Committee on National Certificates in Metallurgy	250 0 0	
—		,, Joint Committee on Metallurgical Education	50 0 0	
—		,, Mond Nickel Fellowships Committee, Administrative Expenses	25 0 0	
—		,, List of Members	330 0 0	
11,430				12,589 8 9
342		,, Excess Expenditure—*Journal*	—	
		,, ,, Special		
17		,, ,, Publications	—	
359				
—	—	,, *Excess of Income over Expenditure for the Year*		883 3 10
£11,789				£13,472 12 7

30.6.47.		INCOME.	£ s. d.	£ s. d.
£	£			
7,791		By Annual Subscriptions		11,218 15 9
		,, Interest on Investments (gross):		
	460	General Fund	725 14 6	
	572	Endowment Fund	638 5 2	
1,032				1,363 19 8
135		,, Profit on Sale of Investments		177 16 2
15		,, Sundry Receipts		34 8 6
—		,, *Publications:*		
		Excess of Income over Expenditure for the year:		
		Journal and *Metallurgical Abstracts*	351 13 5	
		Special Publications	325 19 1	
				677 12 6
2,816		,, *Excess Expenditure for Year*		
£11,789				£13,472 12 7

THE INSTITUTE OF METALS.

PUBLICATIONS ACCOUNTS FOR THE YEAR ENDED 30 JUNE 1948.

JOURNAL AND *METALLURGICAL ABSTRACTS* ACCOUNT.

30.6.47. £	£	EXPENDITURE.	£ s. d.	£ s. d.	30.6.47. £	£	INCOME.	£ s. d.	£ s. d.
		To Stock of *Journals* at 30 June 1947 —nominal value		1 0 0			By Sales of *Journals* and *Metallurgical Abstracts*	3,790 16 7	
1		„ Monthly *Journal*—Production Costs	5,848 1 3			2,939	„ Receipts from Advertisements, *less* Agents' charges	4,009 10 11	
4,372		„ *Journal*—Overprint for Binding	62 18 10			3,482			7,800 7 6
113		„ *Metallurgical Abstracts*—Overprint for Binding	45 2 10		6,421		„ Stock of *Journals* at June 30 1948 —nominal value		1 0 0
270		„ Packing, Despatch, and Postage	747 15 7		1		„ Excess Expenditure for Year		—
593		„ Abstractors and Reviewers Fees	368 1 10		342				
327		„ Miscellaneous Expenditure (including Sales Development)	105 17 6						
100		„ Binding	92 17 4						
311		„ Reprints of Papers	177 18 11						
177									
6,763				7,448 14 1					
—		„ *Excess of Income over Expenditure for the Year*		351 13 5					
£6,764				£7,801 7 6	£6,764				£7,801 7 6

SPECIAL PUBLICATIONS ACCOUNT.

£		£ s. d.	£ s. d.	£		£ s. d.
79	To Royalties on Monographs Nos. 1 and 3	176 2 6		630	By Sales of Special Publications	1,192 15 5
—	„ Reprinting Monograph No. 1	216 5 6		9	„ Interest	—
249	„ Reprinting Monograph No. 3	449 6 5		17	„ Excess Expenditure for Year	—
37	„ Annotated Equilibrium Diagrams	4 1 11				
—	„ Miscellaneous Expenditure	21 0 0				
			866 16 4			
291	„ Mono. No. 4		—			
—	„ *Excess of Income over Expenditure for the Year*		325 19 1			
£656			£1,192 15 5	£656		£1,192 15 5

THE INSTITUTE OF METALS.

FUNDS ACCOUNTS FOR THE YEAR ENDED 30 JUNE 1948.

ENDOWMENT FUND.

30.6.47.	EXPENDITURE.				30.6.47.	INCOME.			
£	£		£	s. d.	£		£	s. d.
		To *Transfer to General Funds:*			*20,292*	By Balance at 30 June 1947	20,986	16 7
	563	Income from Investments	638	5 2	*90*	„ Subscriptions and Donations Received	—	
	8	Income Tax	—		*563*	„ Interest on Investments	638	5 2
571					*3*	„ Bank Interest	1	3 2
20,987		„ Balance at 30 June 1948	21,294	9 10	*610*	„ Profit on Sale of Investments	306	10 1
£21,558			£21,932	15 0	*£21,558*		£21,932	15 0

WAR-TIME EMERGENCY FUND.

£		£	s. d.	£		£	s. d.
—	To Loss on Sale of Investments	11	2 6	*7,767*	By Balance at 30 June 1947	5,143	14 9
2,316	„ Transfer to General Fund	—		*112*	„ Interest on Investments	120	13 1
5,144	„ Balance at 30 June 1948	5,286	16 11	*81*	„ Bank Interest	33	11 7
£7,960		£5,297	19 5	*£7,960*		£5,297	19 5

MOND NICKEL FELLOWSHIPS FUND.

£		£	s d.	£		£	s. d.
—	To Stamp Duty on Deed of Covenant	61	5 0	—	By Balance at 30 June 1947	7,000	0 0
—	„ Printing, Stationery, Postage, and Sundry Expenses	108	0 2	*7,000*	„ Donation Received	7,000	0 0
7,000	„ Balance at 30 June 1948	13,858	11 8	—	„ Interest	27	16 10
£7,000		£14,027	16 10	*£7,000*		£14,027	16 10

CAPPER PASS FUND.

	£	s. d.		£	s. d.
To Balance at 30 June 1948	200	0 0	By Donation Received	200	0 0
	£200	0 0		£200	0 0